CHAPTER IV

STUDY OF ULTRASONIC VELOCITY, DENSITY AND RELATED PARAMETERS IN SOME LIQUID CRYSTALS.

INTRODUCTION:

Ultrasonic techniques are being used increasingly in rece years to study liquid crystals and an intriguing variety effects have been observed. From the knowledge of ultrosor velocity and density the equilibrium properties of the system c be determined, such as the adiabatic compressibility (Ka Moreover, it is also possible to estimate several importa parameters like the molar compressibility (β), the molar sou velocity (R) etc.

[1,2] Rao has made an important advancement in the understandi of molecular structure of liquids. He discovered that the therm coefficient of the velocity of organic liquids is about thr times the thermal coefficient of density. Hence the relation t organic liquids can be written as

$$\frac{dV}{V} = 3\frac{d\rho}{\rho} \quad \ldots\ldots \quad \ldots\cdot(1)$$

Where V is the ultrasonic velocity in the medium and ρ is t density of the liquid. On integrating and simplifying the relati we get

$$\frac{V^{1/3}}{\rho} = K$$

Where K is a constant for a liquid independent of the temperatur Multiplying by the molecular weight this relation takes the form

$$\frac{M}{\rho}(V)^{1/3} = R \quad \ldots\ldots\ldots (2)$$

R is known as the Rao's constant. As M does not vary for particular liquid the quantity $\frac{M}{\rho}(V)^{1/3}$ is constant and called t molar sound velocity. From the extensive study of organic liqui of different homologous series, Rao found that the molar sou velocity is analogous to other physical properties like paracho Sander's viscosity constant and molar refraction. Further it h characteristic values for any one atom or linkage which we deduced by Rao. Rao also found that R is highly constitutive : nature.

Wada[3] found another constant B known as the mol compressibility given by

$$\frac{M}{\rho}\left(K_{ad}\right)^{-1/7} = B \cdots\cdots (3)$$

B is constant for any liquid over a wide range c temperatures. It is termed as the molar compressibility in analog to the molar sound velocity R.

Kad is the adiabatic compressibility given by the relation.

$$\frac{1}{\rho}(v)^{-2} = K_{ad} \cdots\cdots (4)$$

Several investigators have reported anomalous behaviour c the physical properties such as the specific volume, viscocity surface tension, specific heats, ultrasonic velocity ar absorpiton etc near the vicinity of isotropic - mesophase an mesophase - mesophase transitions of the liquid crystals. A ultrasonic velocity is related to the molecular structure ultrasonic studies in the vicinity of the phase transition shoul give a great deal of insight into the mechanism of phas transition in liquid crystals. The density measurements ar necessary for the evaluation of molecular parameters such a adiabatic compressibility. The density measurements, besides bein essential for the determination of order parameter, provide usefu information on the nature of the phase transition ar pretransitional effects. Keeping this in view the ultrasoni velocity and density measurements at different temperatures ha been found experimentally of two/ liquid crystals. The aim of th present investigation is to study the phase transition of thes liquid crystals from the results obtained.

Recently considerable interest has been shown by a number investigators in studying the ultrasonic velocity and density ne the phase transitions of liquid crystals. Review articles b[4] Netale

gives an accumulated data on ultrasonic studies.

Kapustin and Bykona[5] detected the polymesomorphism of liqu crystals by studying ultrasonic velocity and absorpiton in p - - heptyloxy benzoic acid and p - n - octyloxy benzoic acid. Edmonds and Donald[6] have analysed the results of the ultrasonic velocity in P - azoxyanisole reported by Hoyer and Nolle[7] by Frankels[8] heterophase fluctuation theory and by Maier and Saupe[9] long range ordering theory along with absorpiton results by Fixman's[10] theory. Kapustin and Martyanova[11] have reported t measurements of sound velocity and absorption in liquid crysta of homologous azoxy benzenes.

Kartha and Padmini[12] have investigated the behaviours density, ultrasonic velocity, absorpiton and other relat parameters in some cholerteric liquid crystals. They have found anomalies at the isotropic cholesteric phase transition for these parameters. They have analysed the velocity results in the light of Frenkel's theory and absorption results by Fixman's theory. Lord[13] has studied the ultrasonic velocity and absorption in oriented smectic liquid crystals and observed more anisotropy in both absorption and velocity than in oriented nematic liquid crystals. Miyano and Ketterson[14] have measured the ultrasonic velocity and attenuation for magnetically aligned samples of nematic, cholesteric, Smectic B and Smectic C liquid crystals. Otia and Padmini[15] have measured the density and ultrasonic velocity in MBBA and EPAPU and estimated the temperature variation of order parameter S in the nematic phase from the adiabatic compressibility data. Bahadur has made extensive studies of the temperature variation of the specific volume and ultrasonic velocity.[15,16]

Bhattacharya et al[17] have reported strong anomalies in the velocity and attenuation of the longitudinal ultrasound in the vicinity of nematic smectic A transition of TBBA. They have also studied the phase transition in some liquid crystals exhibiting S – S_B and S_A – S_C phase.[18] Measurements of ultrasonic velocity, specific volume and adiabatic compressibility were carried out in some liquid crystals by George and Padmini.[19] The pretransitional effects observed from these quantities were discussed on the basis of de Gennes theory generalized by Bendler.

Rao and Pisipati[20] carried out the concurrent density and ultrasonic velocity studies to detect the phase transition ar pretransitional effects in polymesomorphic liquid crystals. The have calculated the molar sound velocity and molar compressibility in all the phases. It was found that all th transitions are accompained by either an anomaly or sharp rise i the ultrasonic velocity. Recently Rao[21,22] et al have studied th ultrasonic velocity and density in some polymesomorphic liqui crystals. Besides finding the order of the phase transitions the have estimated the pressure dependence of transition temperatu from density measurements.

Experimental

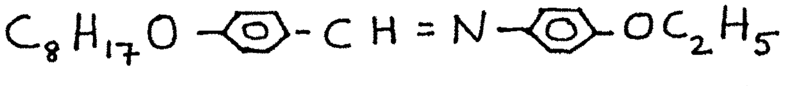
The following liquid crystals were selected for the study.

1. p-n Octyloxybenzylidene - p - Phenetidine (OBP)
2. p- n Octyloxybenzoate p'- methoxyphenyl (OMP)

All the liquid crystals were synthesized in the laboratory.

Synthesis of the liquid crystals.

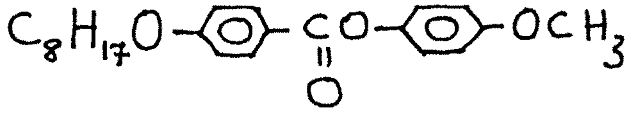
1. The structural formula for OBP is given by



p - Hydroxybenzaldehyde (0.1 mole), dry acetone (100 ml anhydrous K_2CO_3 (0.2 mole) and n - octyl bromide (0.11 mol are introduced into an erlenmeyer fitted with a reflu condenser. The mixture is then stirred vigorously ar heated until reflux. After refluxing for eight hours, th reaction mixture is cooled and then filtered off to remov excess of K_2CO_3 and KBr formed during the reaction. Th precipitate is washed with ether. This filtrate is the evaporated on a rotovapour to obtain p - n - octyloxybenzaldehyde.

OBP is prepared by condensation of P - n - octyloxybenzaldehyde (0.1 mole) and P - phenetidine (0. mole) in refluxing absolute ethanol. After refluxing th reactants for four hours, the solvent is then removed b distillation under reduced pressure and later the pur compound was recrystallized from absolute ethanol until th transition temperature remains constant.

2. The structural formula for OMP is given by



One mole of p - octyloxybenzoic acid was mixed with 2.5 mole o Thionyl chloride and refluxed in a water bath for 8 hours. Th excess of thionyl chloride was removed by directly heating in th flask using the U tube.

Then one mole of p-n Octyloxybenzoyl chloride was added to solution of 1 mole p-methoxyphenol in pyridine. The temperatur kept below 5 to 10 degree C. The solution was stirred for tw hours and kept for 24 hours. After that the solution was added t ice and HCl and filtered. It was than washed with water and col ethanol to remove pyridine. Finally it was washed wit dilute NaOH solution and recrystallized with ethanol

Determination of the transition temperature.

The transition temperatures of liquid crystals can b determined by observing the texture of the sample kept between tw glass slides through an electrically heated hot stage microscope The microscope used in this investigation is a Leitz Laborlux - I Pol. Binocular polarizing microscope equipped with a heatin stage. The temperature of the heating stage can be electricall controlled by a regulator, in the range of room temperature to 36 degree C and can be conveniently read by suitable thermometers The heating state is calibrated by standard organic substances The transition temperatures are recorded by observing the chang in the textures. The transition to isotropic liquid was found whe the field of vision becomes extinct.

Measurements of Ultrasonic Velocity.

The ultrasonic velocity measurments in liquid crystals wer carried out using a double crystal fixed path interferometer. Th experimental set up used for this purpose is schematicall represented in the figure 4.1. It consists of a variable frequenc oscillator, (frequency range 1 MHz to 3 MHz) the interferomete cell with shielded crystal holders and a sensitive vacuum tub voltmeter.

The interferometer cell and its parts are shown in th figure 4.2. The cell is a hollow stainless steel container wit rectangular cross section having dimension of (3x 3x 2.5) cm3 an

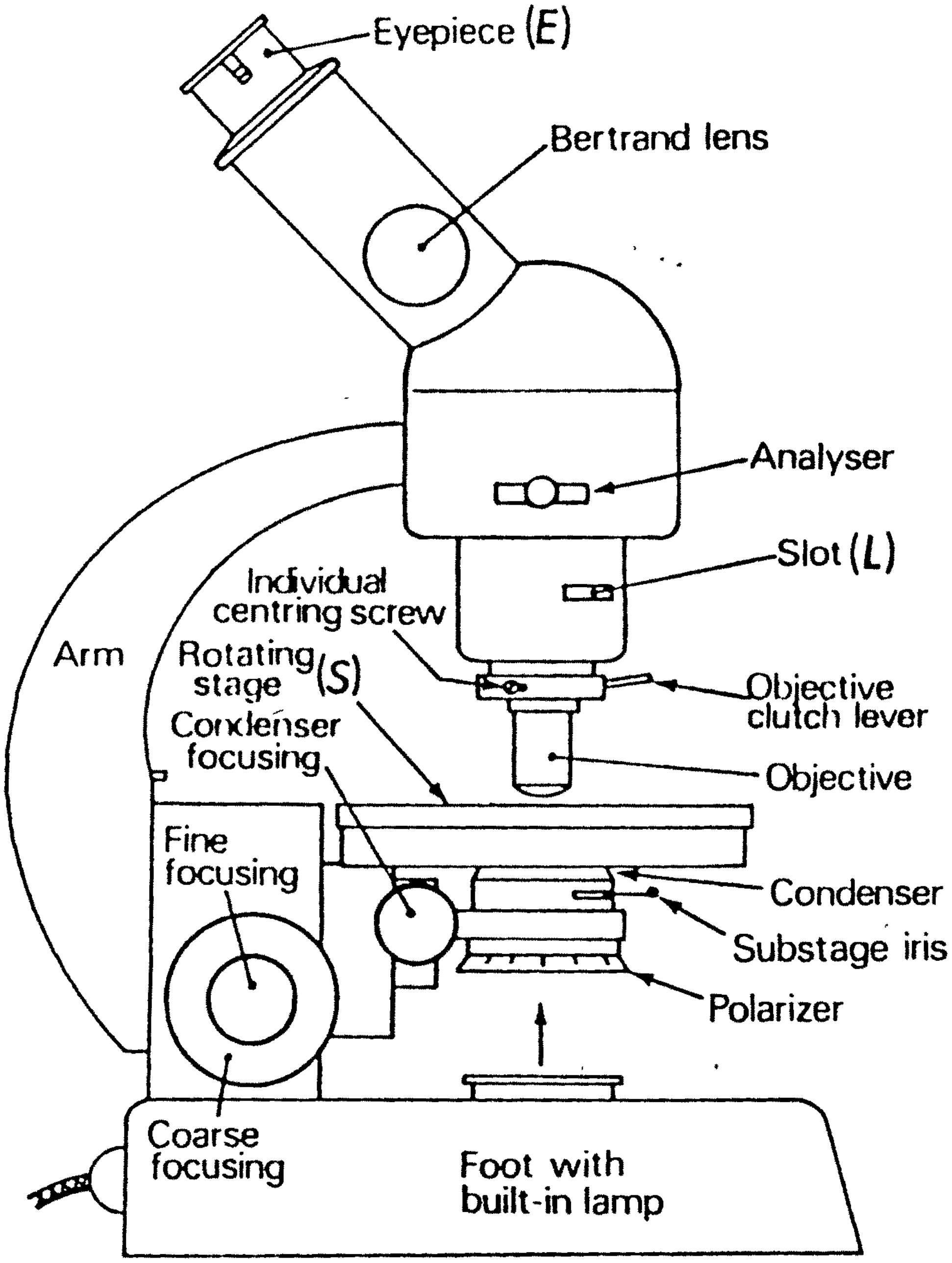


FIG. The polarizing microscope.

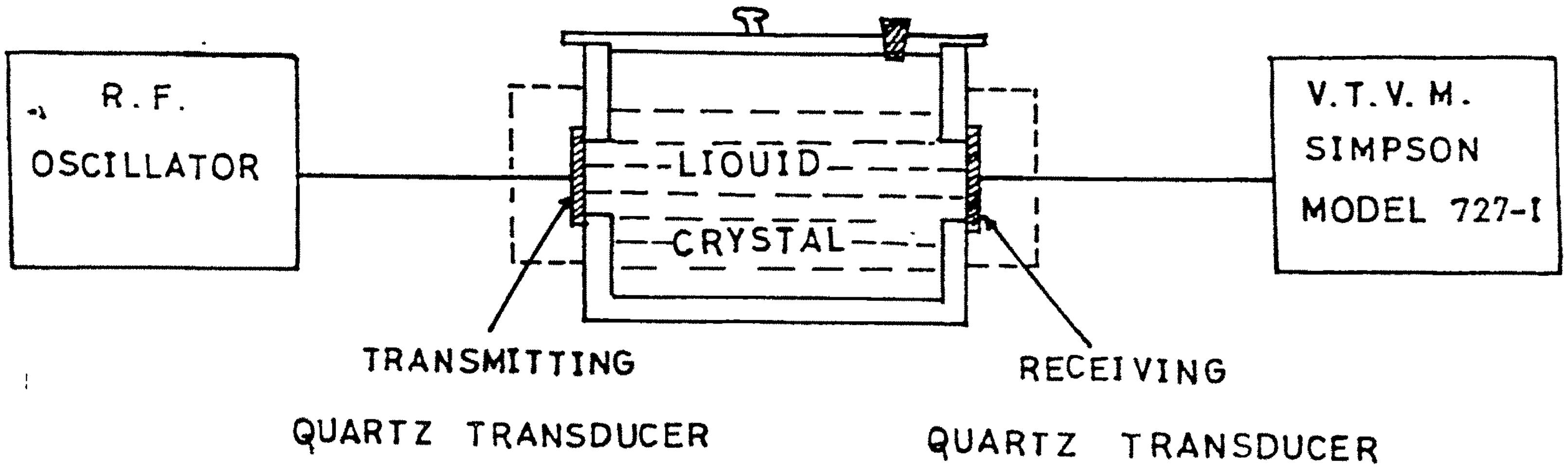


FIG. 4.1 BLOCK DIAGRAM OF CONTINUOUS WAVE ELECTRICAL METHOD

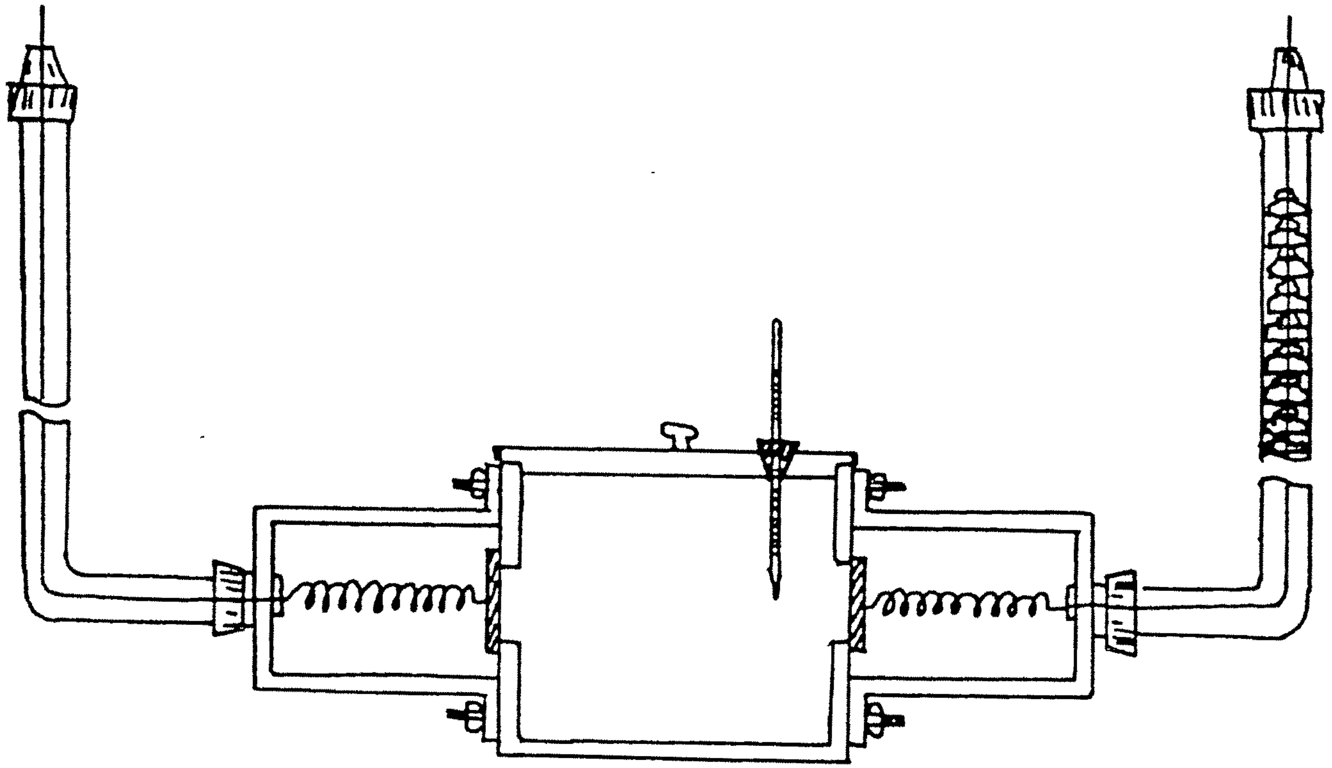


FIG. 4·2· DETAILS OF CELL AND CRYSTAL HOLDER

(NOT TO SCALE)

wall thickness 2mm. A tight lid having a small opening to inser the thermocouple leads for the temperature measurements i provided with the cell. The two opposite sides of the cell ar drilled for holes of 2.2cm diameter. These two sides are machine on precision milling machine for exact parallelism to ± 0.2mm an then finely polished. Two X cut quartz cyrstals of 2 MH fundamental frequency and 2.5 cm diameter are used as transmittin and receiving transducers. These crystals are centrally place over the apertures and fixed with araldite. The faces of th cyrstals are gold plated which serve as electrodes. The shield for the crystals consist of two brass cups sufficient to cover th crystal assembly with rim diameter of about 4mm. It also serve for the earth connection. These cups are fixed to the cell b bolts welded to the four corners each of the two opposite faces o the cell. From the microphone connector fixed to the base of th cup runs a small spring having soldered electrode at the othe end. When the crystal shields are set in position, the metal electrodes from the spring touch the gold plated surface of th cyrstal to establish the electrical contact. A brass pipe of 1 c diameter bent into L shape is coupled to the metal cup b microphone connectors. The cable thorugh the brass pipe is insulated by using porcelain beads.

For the measurement of velocity the liquid crystal sample is taken in the cell and the lid closed. It is then immersed in ar oil bath whose temperature is maintained constant by a circulating thermostat (MLW - U2 Germany) to the accuracy of ± 0.02 degree C. The liquid crystal is heated 10 degree C beyond the anisotropic - isotropic transition temperature and the measurments are taken while cooling. The RF oscillator, frequency meter and the V.T.V.M are switched on and some time is allowed for the preliminary heating and stabilization. At first the condenser of the oscillator is set at a certain frequency which is read by the frequency meter. The frequency is then continuously varied to cover 10 maxima in the V.T.V.M. The procedure is repeated to cover atleast 100 maxima. The ultrasonic velocity at a particular temperature is obtained from the relation $V=2L \times \Delta f$. When Δf is the average value of frequency between two maxima L is determined by measuring Δf for three different standard liquids for which the velocities are known.

The details of density measurement are given Chapter II.

Results and Discussions:

The tabls 4.1 (a), 4.2 (a) show the values of ultrasonic velocity (V) and specific volume (v) at different temperature The parameters adiabatic compressibility Kad, molar sound velocity R and molar compressibility β are calculated and included in the above tables.

Temperature Variation of ultrasonic Velocity (V) and specific volume (v) in OBP:-

Fig.4.1(a) represents temperature variation of ultrasonic velocity and specific volume in the nematic liquid crystal OBP. It

TABLE 4.1 (a)

Variation of v, Kad, R & B with temperature for OBP:

Temp T°C.	Velocity (V) m/sec.	Sp. Volume (v) cm^3/gm.	Ad.Comp. (Kad) x 10^{12} cm/dyne	Molar sound vel. (R)	Molar comp. (B).
112	1211	1.0088	68.79	3801	194.83
113	1208	1.0094	69.17	3801	194.80
114	1206	1.0101	69.45	3801	194.83
115	1204	1.0108	69.73	3801	194.85
116	1198	1.0116	70.49	3798	194.71
116.5	1193	1.0120	71.11	3794	194.55
116.8	1186	1.0122	71.96	3788	194.26
117	1170	1.0133	74.02	3774	193.67
117.2	1181	1.0139	72.69	3788	194.29
117.5	1189	1.0142	71.74	3798	194.72
117.8	1192	1.0144	71.39	3802	194.89
118	1194	1.0147	71.18	3805	195.03
118.4	1195	1.0148	71.06	3807	195.10
118.8	1195	1.0151	71.08	3808	195.15
119.2	1194	1.0153	72.22	3807	195.14
120	1191	1.0158	71.61	3806	195.08
121	1188	1.0164	72.01	3805	195.03

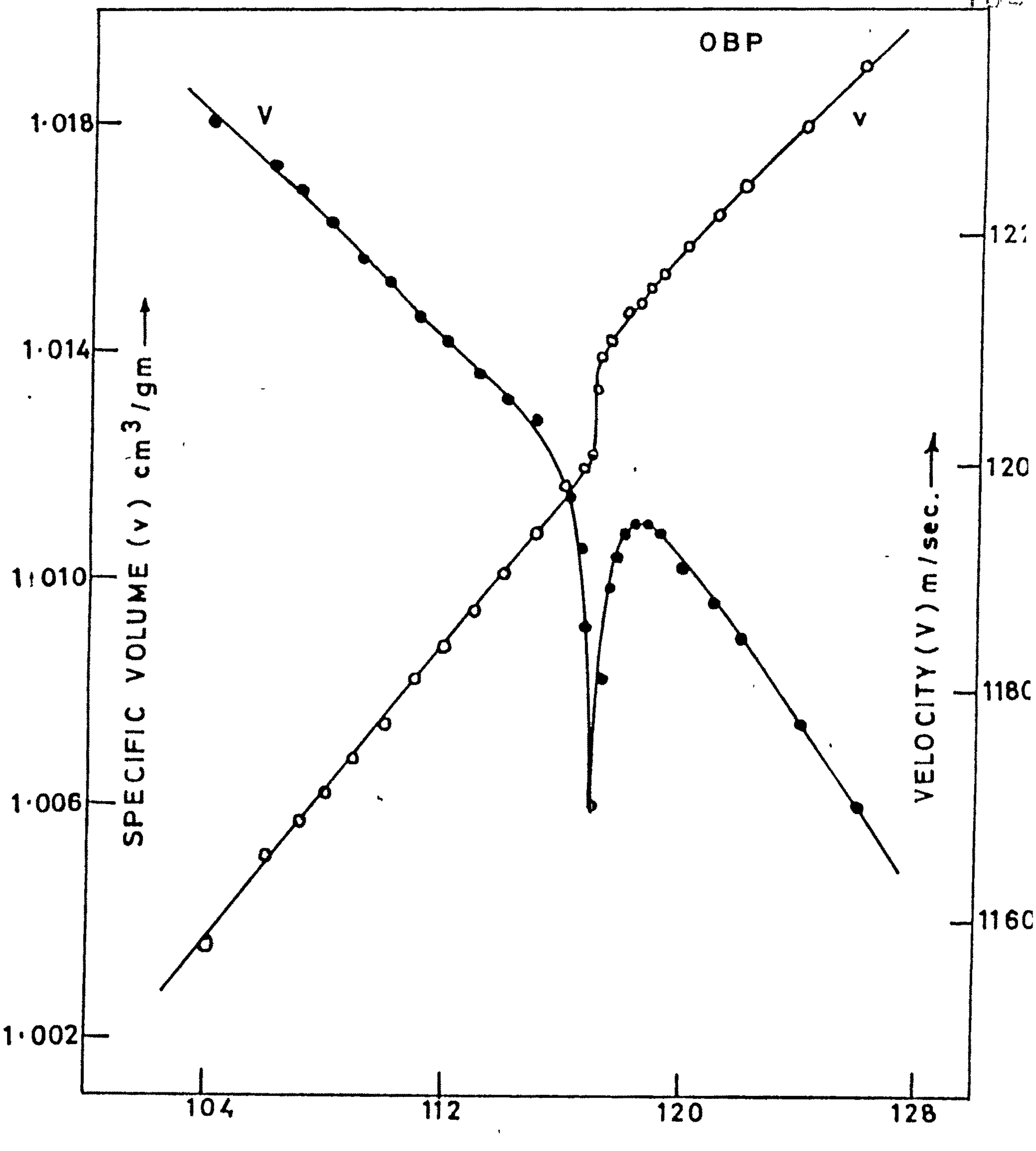

OBP
V
v
1·018
1·014
1·010
1·006
1·002
SPECIFIC VOLUME (v) cm^3/gm
VELOCITY (V) m/sec.
12
120
1180
1160
104
112
120
128
TEMPERATURE (T) °C

FIGURE - 4·1 (a)

can be seen from the figure that the velocity exhibits an anomalous behaviour at the isotropic nematic transition while it varies linearly in the isotropic and nematic phases away from the transition. The velocity shows a dip of 25 m/sec at the phase transition. The specific volume shows the linear variation in both the phases away from the transition, but shows a jump of 0.001 cm^3/gm over a range of 2 degree C in the vicinity of the isotropic nematic phase transition.

Temperature variation of Adiabatic compressibility (Kad) Molar sound Velocity (R) and Molar compressibility (B) in OBP.

Fig 4·1(b)represents the variation of adiabatic compressibility and molar sound velocity with temperature for OBP The variation of adiabatic compressibility is found to be linear in the isotropic and nematic phases, but it shows the maximum of 1.5×10^{-12} $cm^2/dyne$ at the isotropic nematic transition. The molar sound velocity varies linearly in both the phases and shows a dip of 34 at the phase transition. It is intersting to note that R is found to be nearly constant in both the phases away from th transition. A study of the results of molar compressibility shows that B varies linearly in both the phases but exhibits a dip a the nematic - isotropic transition.

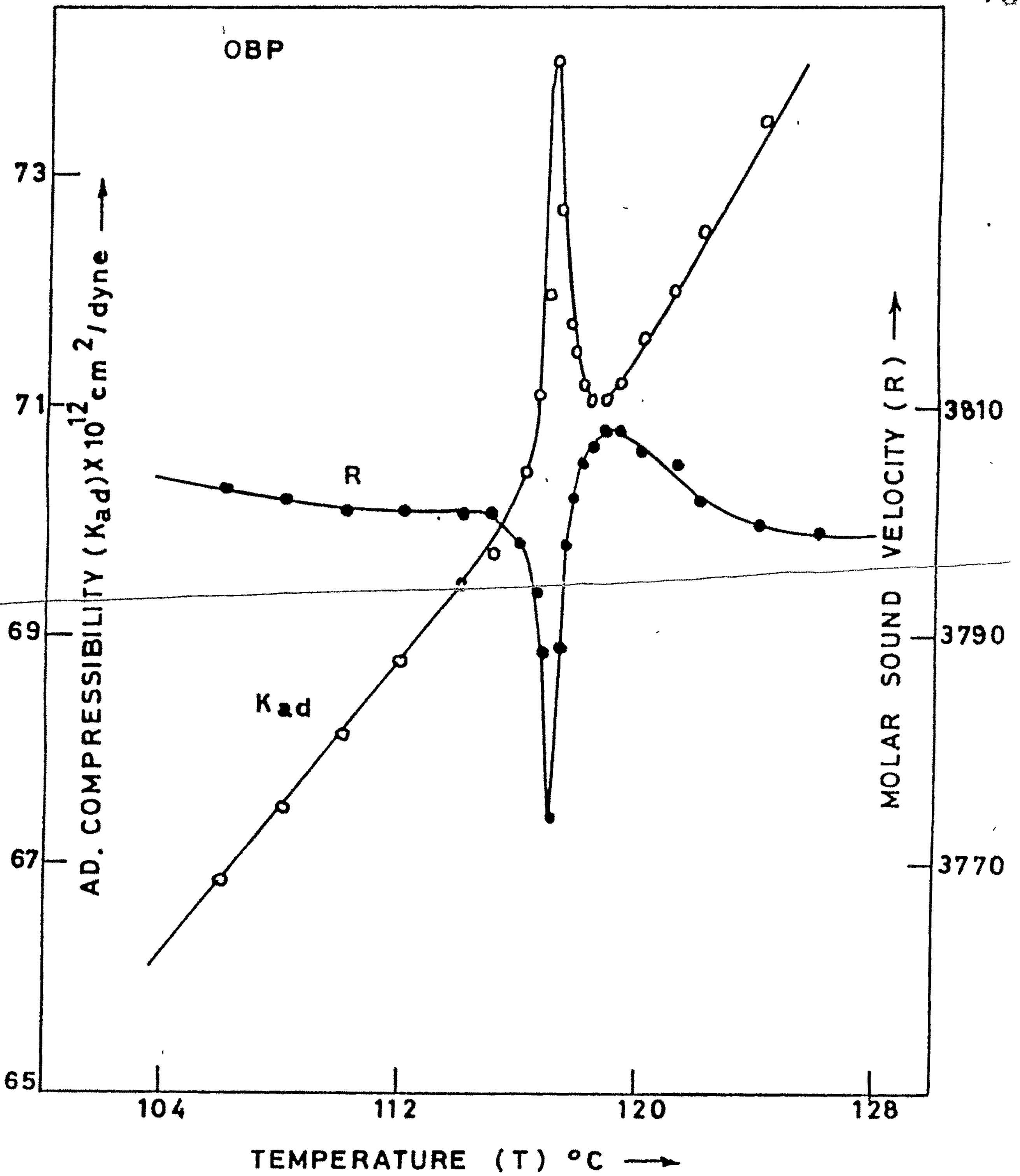

OBP
R
Kad
73
71
69
67
65
104
112
120
128
3810
3790
3770
AD. COMPRESSIBILITY (Kad) X 10^12 cm^2/dyne →
MOLAR SOUND VELOCITY (R) →
TEMPERATURE (T) °C →

FIGURE - 4·1 (b)

Temperature Variation of Ultrasonic Velocity (V) and Specifi Volume (v) in OMP.

Figure 4·2(a) represents the variation of ultrasonic velocity an specific volume in OMP. The velocity exhibits remarkable linea variation both in the anisotropic and isotropic phases away fro transition. A sharp dip of 26 m/sec is observed at the isotropi nematic transition temperature T_{NI}. The jump in the volume at T_{NI} is about 0.003 cm^3/gm within a range of 2 degrees.

Temperature Variation of Adiabatic Compressibility (Kad), Mola Sound Velocity (R) and Molar Compressibility (B) in OMP.

The adiabatic compressibility K_{ad} exhibits analogous behavio with a maxima of about 0.14 $cm^2/dyne$ at T_{NI}. The molar sour velocity shows a dip at the phase transition.

The order parameter S_k is estimated from the specific volume measurements in the nematic and isotropic phase following Mai and Saupe's theory. The volume jump ΔV_k occuring at Tn is estimat by extrapolating the linear plots of specific volume agains temperature curve to the transition temperature. The ratio $\frac{\Delta V_k}{V_{k,n}}$ where $V_{k,n}$ is the volume at the transition is four to be 0.0021 for OBP and 0.0024 for OMP. From the theoritical curve (Maier and Saupe between $\frac{\Delta V_k}{V_{k,n}}$ and S_k the corresponding value of S_k is read. The value of S_k is found to be 0.437 and 0.44 for OBP and OMP respectively. These values are in agreement with the predicted values of S_k by Maier and Saupe for all nematic liquid

TABLE 4.2 (a)

Variation of v, Kad, R & B with temperature for DMP:

Temp T C.	Velocity (V) m/sec.	Sp. Volume (v) $cm^3/gm.$	Ad.Comp. (Kad) x 10^{12} cm/dyne	Molar sound vel. (R)	Molar comp. (B).
71	1350	.9546	52.38	3502.0	184.3
72	1346	.9555	52.74	3501.8	184.3
73	1343	.9564	53.03	3502.5	184.4
74	1341	.9575	53.25	3504.8	184.5
74.5	1339	.9580	53.43	3505.0	184.5
75	1338	.9588	53.56	3507.0	184.6
75.8	1332	.9597	54.09	3505.1	184.5
76.1	1329	.9601	54.36	3504.0	184.4
76.4	1326	.9606	54.63	3503.2	184.4
77	1310	.9625	56.09	3496.1	184.1
77.5	1316	.9637	55.65	3505.7	184.5
77.7	1321	.9640	55.24	3511.2	184.8
78	1327	.9643	54.76	3517.5	185.0
79	1330	.9652	54.56	3524.2	185.3
80	1328	.9659	54.77	3525.7	185.3
81	1326	.9668	54.99	3525.8	185.4
84.4	1322	.9696	55.48	3532.2	185.7

crystals at T_{NI}.

Chandrasekhar et al[24] on the assumption that the molecules execute rotational oscillations of vibrations about the mean orientation, have shown that the mean square vibrational amplitude is given by

$$\bar{\theta}^2 \propto T \rho^{-2/3} V^{-2} \cdots\cdots (5)$$

Where T is the absolute temperature. This result enables one to make a rough estimate of variation of the vibrational amplitude from available ultrasonic data. They have further shown that for rotational oscillations.

$$S \propto \frac{1}{2}\left[\cos^2(\sqrt{2}\,\theta_{rms}) + \cos(\sqrt{2}\,\theta_{rms})\right] \cdots (6)$$

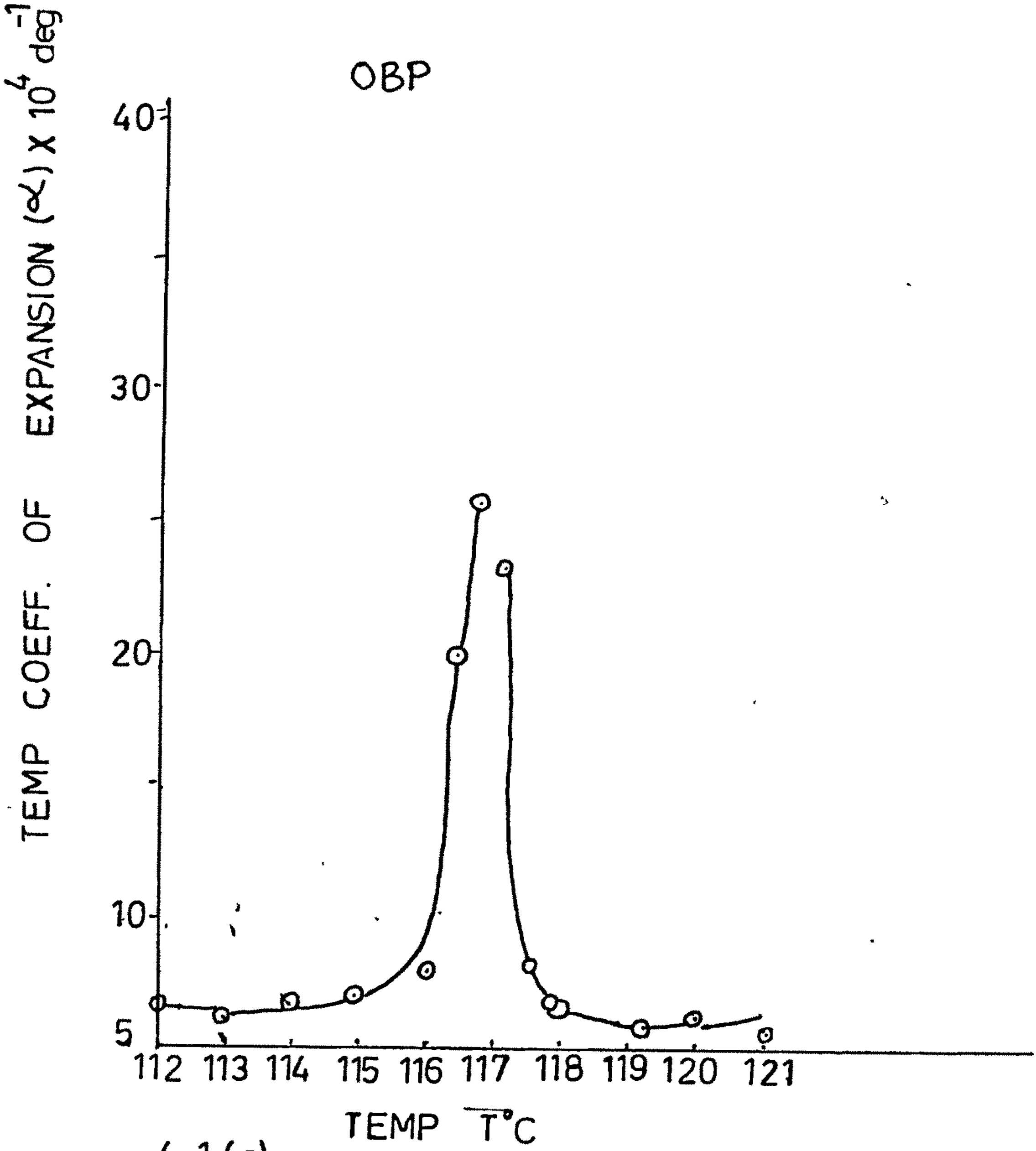
When $\theta_{rms} = (\bar{\theta}^2)^{1/2}$. From equations 5&6 since S_k the order parameter at transition is known, the temperature variation of S is estimated in the nematic region. It is noticed that the trend of variation in S in both compounds is the same, S increases very sharply in the vicinity of Tn and thereafter more gradually. The temperature variation of S in case of OBP is found to be less in comparison to the S value obtained from refrative index data using the Neugabeaur's relation[25].

The termal coefficient of expansion α_T and temperature coefficient of adiabatic compressibility β_T for the two samples are estimated in the isotropic and anisotropic regions on both sides of the transition Tni and their values given in tables in 4.1 (b) and 4.2 (b) are estimated from the specific volume data at different temperatures using $\alpha_T = \frac{1}{v_0}\frac{dv}{dT} \cdots\cdots (7)$

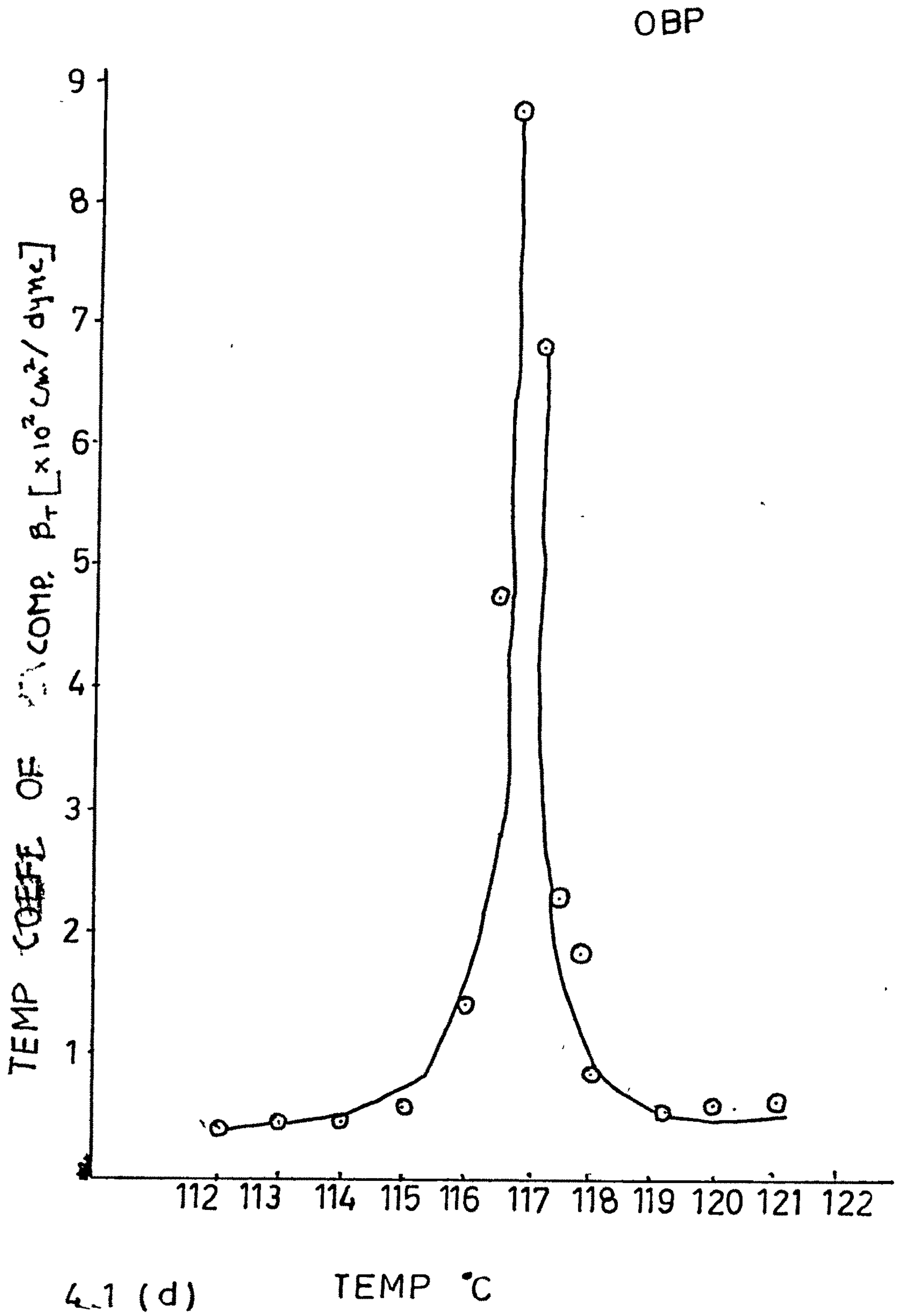
TABLE 4.1 (b)

Variation of α_T and β_T with Temperature for OBP.

Temp T°C	Temp. coeff. of expansion α_T [x 10^{4} deg^{-1}]	Temp. coeff. of ad. comp. β_T [x10^{12} deg.$^{-1}$]
112	6.78 x 10^{-4}	.39
113	6.28	.45
114	6.73	.44
115	6.91	.56
116	8.11	1.42
116.5	19.74	4.73
116.8	25.66	8.78
117.2	23.03	6.76
117.5	7.90	2.25
117.8	6.58	1.80
118	6.51	.84
119.2	5.99	.56
120	6.17	.63
121	5.55	.63


OBP
TEMP COEFF. OF EXPANSION (α) x 10⁴ deg⁻¹
40
30
20
10
5
112
113
114
115
116
117
118
119
120
121
TEMP T°C

4.1 (c)


OBP
TEMP ~~COEFF~~ COEFF OF COMP. β_T [$\times 10^2$ cm^2/ dyne]
9
8
7
6
5
4
3
2
1
112
113
114
115
116
117
118
119
120
121
122
TEMP °C

4.1 (d)

Table 4.1 (c)

Variation of Orms and S with Temperature for OBP.

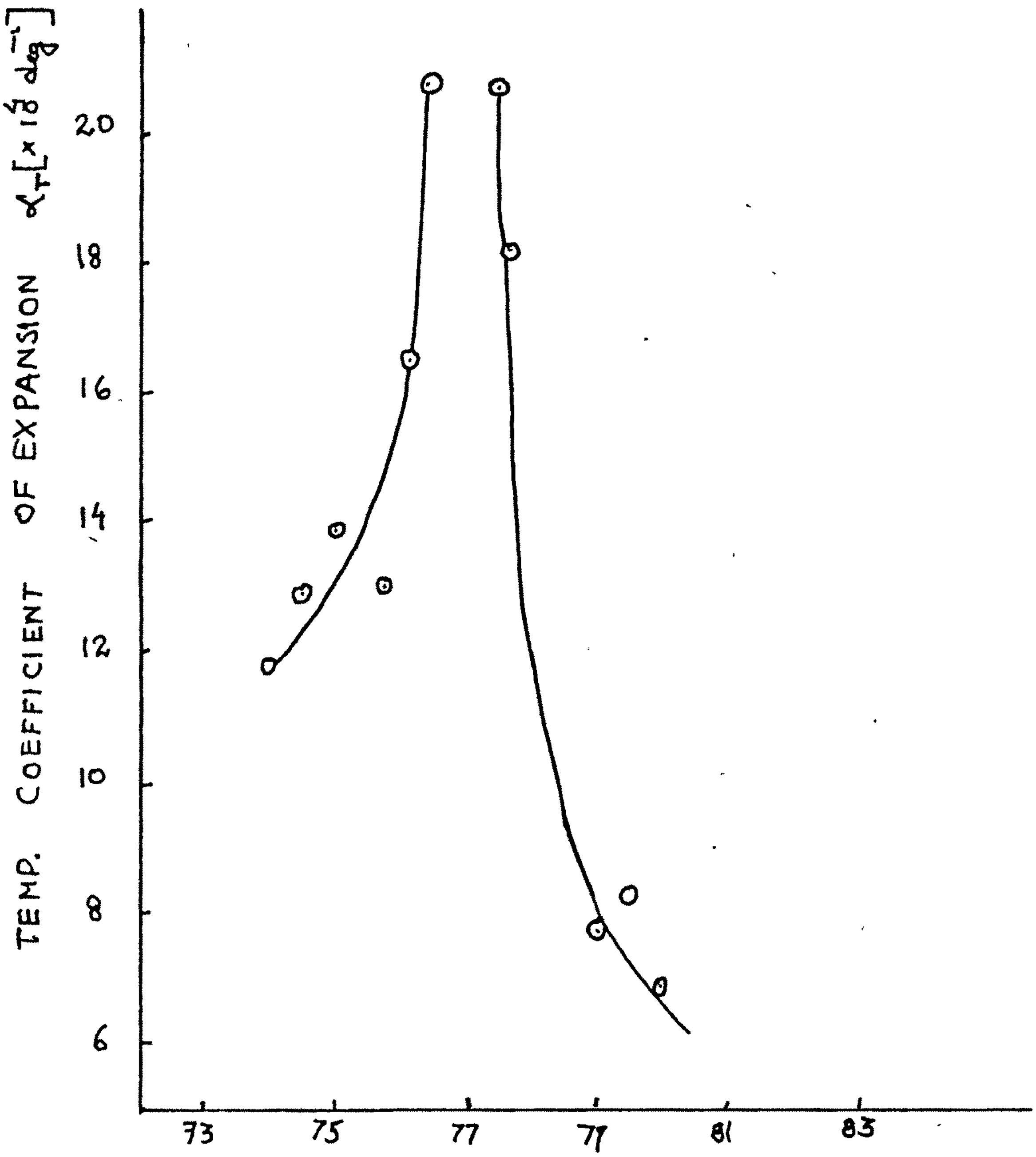
Temp C T	Density ρ gm/cc	Velocity V m/sec	Orms degree	Order para S.
106	.9950	1226	37.2	.48
108	.9938	1221	37.5	.48
110	.9927	1216	37.8	.47
112	.9913	1211	38.1	.47
114	.9900	1206	38.3	.46
116	.9988	1198	38.7	.45
117	.9867	1170	40.0	.43

TABLE 4.2 (b)

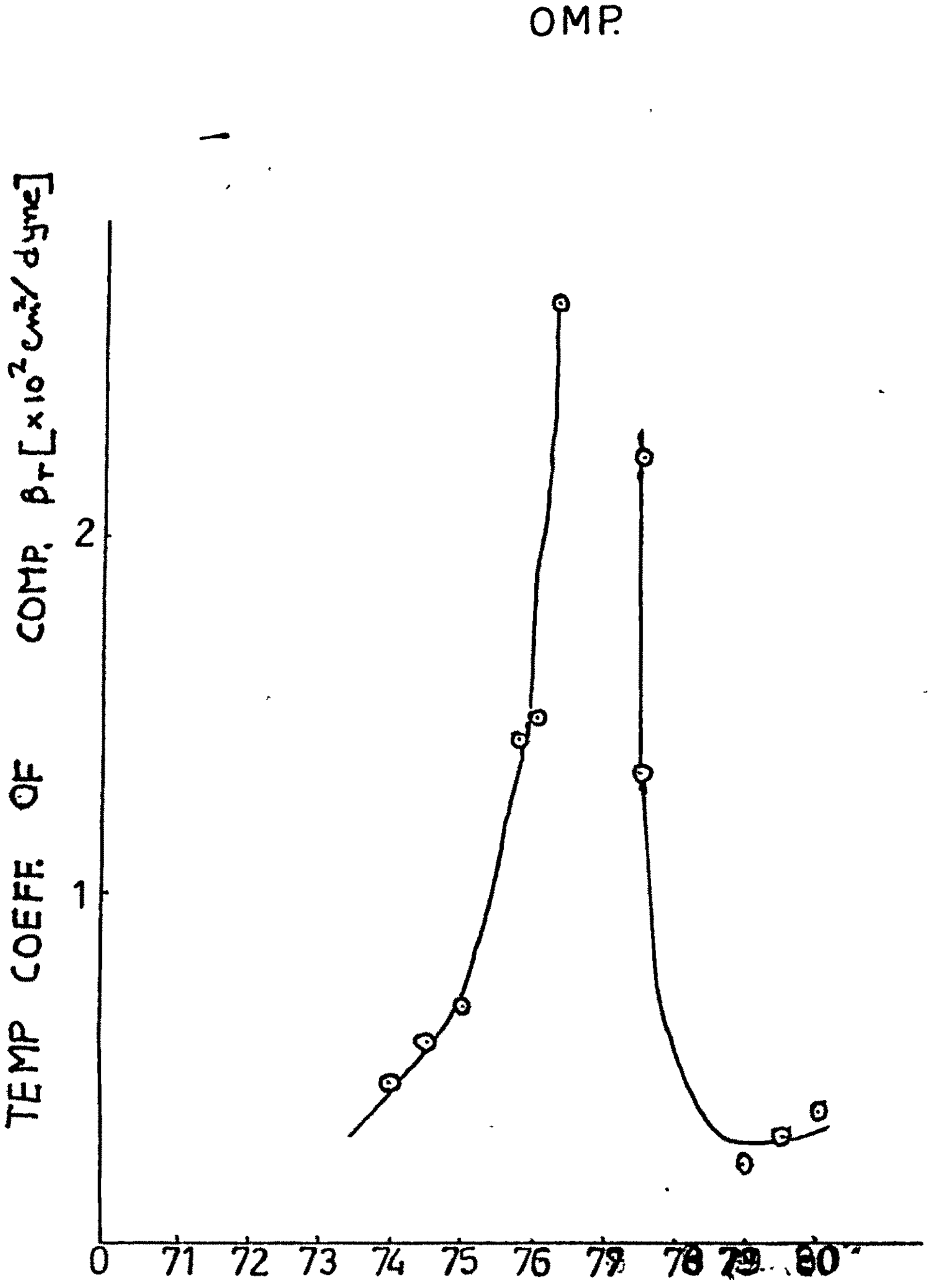
Variation of α_T and β_T with Temperature for OMP.

Temp $T^{\circ}C$	Temp. coeff. of expansion α_T [x 10^{4} deg $^{-1}$]	Temp. coeff. of ad. comp. β_T [x10^{12} deg.$^{-1}$]
74	11.87	0.44
74.5	12.99	0.56
75	13.85	0.67
75.8	12.99	1.43
76.1	16.62	1.49
76.4	20.78	2.67
77.5	20.78	2.23
77.7	18.18	1.33
79	7.79	0.22
79.5	8.31	0.30
80	6.93	0.39

(OMP)



4.2(C) TEMP T°C


OMP.
TEMP COEFF. OF COMP. β_T [× 10^2 cm²/ dyne]
1
2
0
71
72
73
74
75
76
77
78
79
80

4.2 (d) TEMP T C

TABLE 4.2 (c)

Variation of Orms and S with Temperature for OMP.

Temp C T	Density ρ gm/cc	Velocity V m/sec	Orms degree	Order para S.
71	1.0476	1350	37.8	.48
72	1.0466	1346	38.0	.47
73	1.0456	1343	38.15	.47
74	1.0444	1341	38.3	.47
74.5	1.0438	1339	38.4	.46
75	1.0430	1338	38.4	.46
75.8	1.0420	1332	38.7	.46
76.1	1.0416	1329	38.8	.45
76.4	1.0410	1326	38.9	.45
77	1.0390	1310	39	.44

When V_0 is taken at the mid point of the specific volume curve when it rises near the transition. β_T is estimated from the values of Kad at different temperatures, using the relation.

$$\beta_T = \frac{1}{K^{o}_{ad}} \frac{d K_{ad}}{dT} \quad \ldots\ldots (8)$$

o

Where Kad is taken at the temperature near the transition where Kad has its peak value. It is found that from the figures both the parameters attain very high values near the transition indicating the presence of strong pretransition effects. Padmini[17] has given an explanation for the pretransitional effects in the thermal coefficient of expansion and temperature coefficient of adiabatic compressibility in the light of de Genne's theory[26] generalized by Bendler.[27]

Bendler has predicted that the number density flunctuations which are governed by order fluctuations will vary with temperature above nematic transition as $(\Delta\rho)^2 \sim (T-T^*)^{-\gamma} \ldots (9$ where T^* is the pseudo critical temperature of the nematic ordering and γ is the component determining the growth of the order fluctuations.

Bendler has suggested that these density fluctuation produce an increase in isothermal compressibility and the compressibility anomaly is the sole origin of the expansion anomaly.

REFERENCES

1. Rao, M.R. Ind. J.Phys. 14, 109 (1940)

2. Rao M.R., J. Chem. Phys. 9, 682 (1941)

3. Wada Y, J.Phys. Soc. Jpn. 4, 280 (1949)

4. Netale G.G. J. Acous Soc. Amer. 63, 1265 (1978)/65, 1677 (1978)

5. Kapustin, A.Pand Bykoua, N.t. Sov, Phy. Crystallogr. 13, 281 (1968)

6. Edmonds, Peter, D. and Doneld, A Orr. Mol. Cryst. 2, 526 (1966) 2, 135 (1967)

7. Hoyer, W.A and Nolle, A.W. J. Chem. Phys. 24, 803 (1956)

8. Frenkel, J. Kinetic Theory of Liquids, Dover Publications Inc New York, 382 (1946)

9. Maier, W and Saupe, A. Z. Naturfous., 13 A, 564 (1958) 14 A, 882, (1959), 15 A, 287 (1960).

10 Fixman, H. J.Chem. Phys. 36, 1961, (1962)

11 Kapustin, A.P and Martiyanona, L.I. Soc. Phys. Crystalloge. 16, 559 (1971)

12 Kartha, G. G and Padmini, A.R.K.L. J. Phy. Soe. J 31, 90 (1971)

13 Lord, A.E. Phys. Rev. Lett. 29, 1336 (1972)

14 Miyano K and Ketterson J.B. Phy. Rev. A 12 (2) 615 (1975)

15 Bahadur, B.Austica, 33, 278, (1975) 34, 86 (1975)

16 Behadur, B. J. Chem. Phys. 73, 255 (1976)

17 Bhattacharya, S. Sarma, B.K. and Kelterson, J.B. Phys. Rev Lett. 40, 1582 (1978)

18 Bhattacharya, s. Cheng, B.Y. Sarma, B.K. and Ketterson, J.B Phys. Rev. Lett. 49, 1012 (1982)

19 George, A.K. and Padmini, A.R.K.L. ultrasonics Nov. 27, (198

20 Rao N.V.S. and Pisipati, V.G.K.M. Acustica 54, 56 (1983) 5
74 (1984)

21 Pisipati, V.G.K.M. Rao, N.V.S, Gouri Sankar, Y and Murt
J.S.R. Acustica 60, 163, (1986).

22 Rao, N.V.S. Pisipati, V.G.K.M. Prasad, P.V. Datta, a
Alapati, P.R. Mol. Cryst. Liq. Cryst. 136, 307 (1986)

23 Rao, K.S and Rao, B.R. J Sci. Ind. Res. 16 B, 483, (1957)

24 Chandrasekhar, S. Krishnamurti, D., Madhusudana N.V. Mo
Cryst. Liq. Cryst. 8, 45, (1969)

25 Mahajan H.K. Thesis submitted to the M.S. Uni. Baroda Ja
1988.

26 De. Gennes, P.G. Mol. Cryst. Liq. Cryst. 12, 93 (1971)

27 Bendler J. Mol. Cryst. Liq. Cryst. 38, 19 (1977)

Mol Cryst Liq Cryst, 1985, Vol 126, pp 269–279
0026-8941/85/1264–0269/$20 00/0

Refractive Indices and Dielectric Studies of Three Phenylcyclohexane Liquid Crystals in the Nematic Phase

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The refractive indices n_e, n_o and densities and the dielectric primittivities $\epsilon_\parallel$ and $\epsilon_\perp$ of three P-cyano-P′-alkylcyclohexanes (PHC-3, PCH-5, PCH-7) have been measured at different temperatures The order parameters calculated by using Neugebauer and Vuks' methods were comparable A comparison of order parameters of the PCH with the corresponding alkylcyanobiphenyls at reduced temperatures τ (= $T - T_{NI}/T_{NI}$) shows that the replacement of a phenyl ring with a cyclohexyl ring decreases the order parameter appreciably The experimental values of dielectric permittivities $\epsilon_\parallel$ in each of the PCHs are found to be less than half of the $\epsilon_\parallel$-value calculated from Maier and Meier equations using the polarizability and the order parameter obtained from refactive index measurements This was explained as due to short range antiparallel ordering of strongly polar molecules in the nematic phase, as proposed by Chandrasekhar and Madhusudan, which was not taken into consideration in Maier and Meiers' theory

INTRODUCTION

In a recent communication[1] the orientational order parameters of several alkyl and alkoxy cyanobiphenyls were determined from the refractive indices and density measurements using the methods due to Neugebauer,[2] Vuks[3] and Saupe and Maier.[4] The results obtained by Neugebauer and Vuks methods were comparable and agree with those reported from other methods. The object of the present investigations was to study how the order parameter changes with replacement of a phenyl ring in cyanobiphenyls by a cyclohexane ring. It was also intended to study the dielectric permittivities $\epsilon_\parallel$ and $\epsilon_\perp$ parallel and perpendicular to the long axes of PCH molecules and compare these experimental $\epsilon_\parallel$ and $\epsilon_\perp$ values with the $\epsilon_\parallel$ and $\epsilon_\perp$ values calculated from Maier and Meier equations using polarizability α and order parameter S obtained from refractive index measurements. The results are discussed in the paper.

EXPERIMENTAL

The transition temperatures of different mesophases of three P-cyano-P′-alkylcyclohexanes (PCH) obtained from Merck, Germany, are given below.

1. P-cyano-P′-propylphenylcyclohexane (PCH-3): $\xrightarrow{43^\circ C}$ N $\xrightarrow{45^\circ C}$ I
2. P-cyano-P′-Pentylphenylcyclohexane (PCH-5). C $\xrightarrow{30^\circ C}$ N $\xrightarrow{55^\circ C}$ I
3. P-cyano-P′-heptylphenylcyclohexane (PCH-7): C $\xrightarrow{30^\circ C}$ N $\xrightarrow{57^\circ C}$ I

The liquid crystals were used in the investigations without further purification

The method of measurements of the refractive indices n_e, n_o for extraordinary and ordinary ray with the help of ABBE refractometer and the density measurements by means of a capillary tube method were described earlier [1]

Measurements of dielectric permittivities $\epsilon_\parallel$ and $\epsilon_\perp$ were made with a GR-1620 capacitance bridge using a capacitor of stainless steel electrodes separted by 1 mm teflon spacer described earlier.[5] Alignment of molecules parallel and perpendicular to the electrode surfaces were made by 10 KG magnetic field. The cell was calibrated with freshly distilled toluene and chlorobenzene and values agreed to 0 1% of the standard value. The temperature of the cell was maintained constant by means of a thermostat.

RESULTS

The experimental values of refractive indices n_e, n_o and the densities of the liquid crystals at different temperatures are given in Tables (I–III) The refractive index anisotropy is shown in figure 1 (a, b, c). The effective polarizabilities α_e and α_o in the nematic phase were

TABLE I

Refractive indices density and order parameter S for PCH-3

					Vuks Method			Neugebauer's Method		
$T\,^0C$	n_o	n_e	$\rho gm/cc$	$\bar{\alpha}(\dot{A}^3)$	$\alpha_o(\dot{A}^3)$	$\alpha_e(\dot{A}^3)$	S	$\alpha_o(\dot{A}^3)$	$\alpha_e(\dot{A}^3)$	S
42	1 4912	1 5852	0 9685	28 39	26 31	32 54	0 67	26 66	31 85	0 63
42 5	1 4913	1 5842	0 9678	28 40	26 35	32 50	0 66	26 69	31 82	0 63
43	1 4920	1 5820	0 9672	28 40	26 41	32 38	0 64	26 75	31 71	0 61
43 5	1 4920	1 5814	0 9666	28 41	26 43	32 36	0 64	26 76	31 70	0 60
44	1 4928	1 5787	0 9660	28 41	26 51	32 21	0 61	26 83	31 58	0 58
44 5	1 4930	1 5775	0 9652	28 42	26 55	32 16	0 60	26 86	31 54	0 57
45	1 4936	1 5755	0 9645	28 43	26 61	32 05	0 58	26 91	31 45	0 55
46iso	1 5208		0 9576							
46 5	1 5205		0 9571							
47	1 5201		0 9567							
47 5	1 5200		0 9560							
48	1 5197		0 9555							

$\alpha_{11} = 34\ 82$ $\alpha_\perp = 25\ 49$ $\alpha_{11} = 34\ 06$ $\alpha_\perp = 25\ 87$

calculated using two methods, Neugebauer and Vuks and are included in the Tables (I–III). The principal polarizabilities $\alpha_{\|}$ and $\alpha_\perp$ parallel and perpendicular to the long axis of molecules in the crystalline state were obtained from Hallers' et al.[6] graphical method The order parameter S calculated from the relation $S = (\alpha_e - \alpha_o)/(\alpha_{\|} - \alpha_\perp)$, are also included in Tables (I–III).

TABLE II

Refractive indices, density and order parameter S for PCH-5

					Vuks Method			Neugebauer's Method		
$T\,^0C$	n_o	n_e	$\rho gm/cc$	$\bar{\alpha}(\dot{A}^3)$	$\alpha_o(\dot{A}^3)$	$\alpha_e(\dot{A}^3)$	S	$\alpha_o(\dot{A}^3)$	$\alpha_e(\dot{A}^3)$	S
31	1 4870	1 6000	9610	32 26	29 44	37 92	0 63	29 92	36 95	0 65
33	1 4864	1 5979	9593	32 27	29 47	37 85	0 62	29 94	36 91	0 65
35	1 4860	1 5953	9582	32 24	29 50	37 72	0 61	29 97	36 79	0 63
37	1 4860	1 5918	9565	32 23	29 57	37 55	0 59	30 03	36 65	0 61
39	1 4860	1 5880	9548	32 24	29 65	37 35	0 57	30 05	36 60	0 61
41	1 4860	1 5849	9529	32 23	29 74	37 21	0 56	30 16	36 38	0 58
43	1 4860	1 5815	9512	32 23	29 81	37 05	0 54	30 22	36 23	0 56
45	1 4860	1 5783	9492	32 24	29 90	36 90	0 52	30 29	36 13	0 55
47	1 4860	1 5746	9473	32 23	29 99	36 72	0 50	30 37	35 96	0 52
49	1 4860	1 5711	9451	32 25	30 08	36 56	0 48	30 42	35 89	0 51
51	1 4870	1 5654	9423	32 27	30 28	36 26	0 44	30 61	35 59	0 46
54	1 4898	1 5554	9389	32 21				30 91	35 10	0 39
56iso	1 5105		9336							
58	1 5095		9317							
60	1 5081		9300							
63	1 5075									

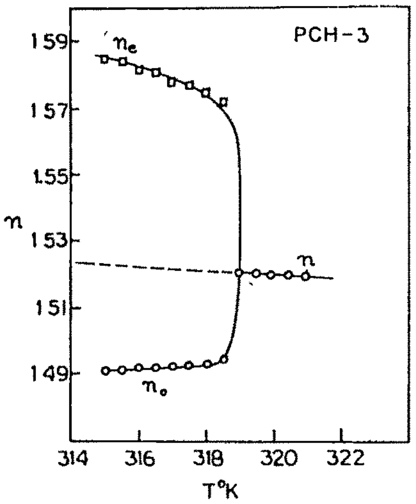
$\alpha_{11} = 41\ 38$ $\alpha_\perp = 27\ 92$ $\alpha_{11} = 39\ 60$ $\alpha_\perp = 28\ 81$

TABLE III

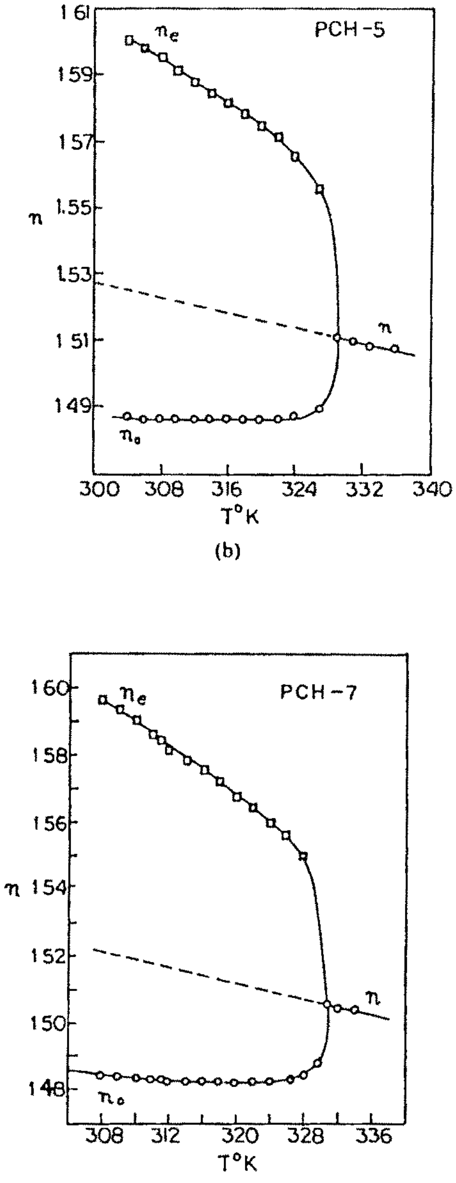
Refractive indices, density and order parameter S for PCH-7

					Vuks Method			Neugebauer's Method		
T^0C	n_o	n_e	$\rho gm/cc$	$\bar{\alpha}(\dot{A}^3)$	$\alpha_o(\dot{A}^3)$	$\alpha_e(\dot{A}^3)$	S	$\alpha_o(\dot{A}^3)$	$\alpha_e(\dot{A}^3)$	S
31	1 4840	1 5964	.9499	36 68	33 46	43 10	0.60	34.01	42.01	0 58
33	1 4838	1.5934	9489	36 64	33 51	42.91	0 59	34.04	41 85	0 57
35	1 4836	1.5903	.9467	36.66	33 60	42 77	0 57	34.12	41.74	0.55
37	1 4832	1.5867	.9445	36.65	33 68	42.60	0.56	34.18	41.60	0.54
38	1.4830	1.5842	.9429	36 66	33 74	42 48	0 55	34 23	41 51	0.53
39	1 4825	1 5814	.9411	36 65	33.80	42 35	0 53	34 34	41 26	0 50
41	1 4822	1.5783	.9394	36 64	33 87	42 19	0 52	34.34	41 24	0 50
43	1.4820	1.5752	9375	36 64	33 95	42 03	0 50	34.40	41.12	0 49
45	1 4820	1.5720	.9355	36 65	34 05	41 87	0.49	34.49	40 97	0.47
47	1.4820	1 5679	9335	36 65	34 15	41 63	0 47	34 56	40 83	0.46
49	1 4820	1.5645	.9316	36 65	34.43	41.45	0 44	34 66	40 63	0 43
51	1 4822	1 5598	.9293	36 65	34 39	41 17	0.42	34 77	-40.40	0 41
53	1.4830	1 5559	9268	36 70	34 57	40 96	0 40	34 93	40 23	0 39
55	1 4842	1 5498	.9205	36.87	34 94	40 72	0.36	35 26	40.08	0 35
57	1 4876									
58iso	1 5055									
59	1 5040									
61	1 5035									

$\alpha_{\parallel} = 47\ 64$ $\alpha_{\perp} = 31.62$ $\alpha_{\parallel} = 46.14$ $\alpha_{\perp} = 32\ 36$



(a)



(b)

(c)

FIGURE 1a, 1b, 1c Refractive index anisotropy plots for PCH-3, PCH-5, PCH-7 respectively

TABLE IV

Values of $\epsilon_\parallel$, $\epsilon_\perp$ and order parameter S from dielectric anisotropy values

	T^0C	$\epsilon_\parallel$	$\bar{\epsilon}$	$\epsilon_\perp$	$\Delta\epsilon$	S from $\Delta\epsilon$ values
	43	16.58		6.90	9.68	0.20
	43.5	16.21		7.02	9.19	0.19
PCH-3	44	15.98		7.06	8.92	0.18
	44.5	15.74		7.25	8.49	0.18
$\mu_D = 4.98$	45	15.51		7.49	8.02	0.17
	45 iso		10.62			
	47		10.65			
	49		10.71			
	33	14.74		4.81	9.93	0.32
	35	14.51		4.97	9.54	0.31
PCH-5	39	14.38		5.20	9.18	0.30
$\mu_D = 4.27$	43	14.23		5.40	8.83	0.29
	48	13.92		5.69	8.23	
	52	13.32		6.08	7.24	
	56 iso		8.93			
	58		9.02			
	60		9.06			
	31	12.85		4.18	8.67	0.31
	35	12.63		4.30	8.33	0.30
PHC-7	39	12.53		4.41	8.12	0.29
	43	12.37		4.53	7.84	0.29
$\mu_D = 4.39$	48	12.21		4.80	7.41	
	52	12.03		5.11	6.92	
	56	11.74		5.71	6.03	
	59 iso		8.69			
	61		8.76			
	63		8.82			

The experimental values of the dielectric permittivities $\epsilon_\parallel$ and $\epsilon_\perp$ of the liquid crystals in the nematic phase are given in Table IV. The calculated values $\epsilon_\parallel$ and $\epsilon_\perp$ obtained from the Maier and Meier equations[7] are included in Table IV.

Maier and Meiers' equations are

$$\epsilon_\parallel = 1 + 4\pi NhF\left[\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu^2}{3kT}\left\{1 - (1 - 3\,\mathrm{Cos}^2\beta)\right\}S\right] \qquad (1)$$

$$\epsilon_\perp = 1 + 4\pi NhF\left[\bar{\alpha} - \frac{1}{3}\Delta\alpha S + \frac{F\mu^2}{3kT}\left\{1 + \frac{1}{2}(1 - 3\,\mathrm{Cos}^2\beta)\right\}S\right] \qquad (2)$$

$$\Delta\epsilon = 4\pi NhF\left[\Delta\alpha - \frac{F\mu^2}{2kT}(1 - 3\,\mathrm{Cos}^2\beta)\right]S \qquad (3)$$

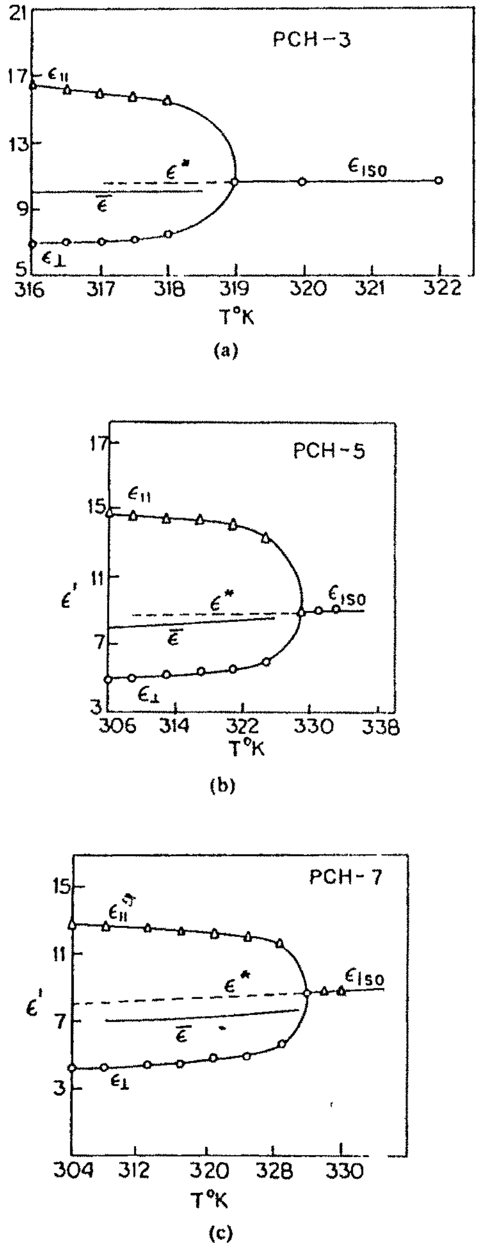


FIGURE 2a, 2b, 2c Dielectric anisotropy plots for PCH-3, PCH-5, PCH-7 respectively where N is the number of molecules per c.c.; $h = 3\bar{\epsilon}/2\bar{\epsilon} + 1$, cavity field factor; $F = 1/1 - \bar{\alpha}f$, Reaction field factor; $f = 4\pi N(2\bar{\epsilon} - 2)/3(2\bar{\epsilon} + 1)$; μ is the dipole moment of free molecule; $\Delta\alpha$ = polarizability anisotropy; $\Delta\epsilon$ = dielectric anisotropy.

The dipole moment μ of the liquid crystals were determined in dilute solution in benzene and are included in Table IV. Dielectric anisotropy is shown in figure 2 (a, b, c).

DISCUSSION

It can be seen from Tables (I–III) that the order parameter S of the liquid crystals PCH-3, PCH-5 and PCH-7 obtained from the refractive indices data using the Neugebauer and Vuks methods are comparable. The order parameter for PCH-7 obtained in the present investigation agrees well with that obtained from dimagnetic susceptibility reported earlier.[8] It can be seen from fig. 3(a, b) that the order parameter of PCH-5 and PCH-7 at any reduced temperature $\tau = (T - T_{NI})/T_{NI}$ is less than the S-value of the corresponding Pentyl and heptylcylanobiphenyl at the same reduced temperature. It is therefore concluded that the replacement of a phenyl ring in cyanobiphenyls by a cylohexyl ring reduces the order parameter appreciably. The values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ obtained in this study are fairly in agreement with those obtained by Pohl et al.[9]

From fig 2(a, b, c) it can be seen that the average dielectric constant $\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ is always less than the dielectric constant ϵ^*_{is} at $T < T_{NI}$ extrapolated in the nematic range from ϵ_{iso} at $T > T_{NI}$ in all

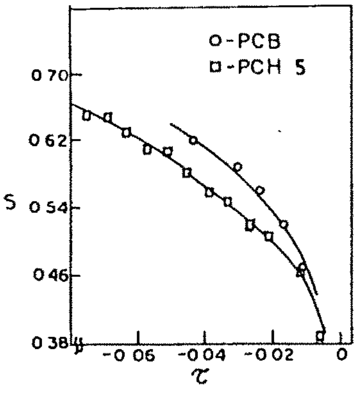


FIGURE 3a Plots of order parameter S vs τ for PCB and PCH-5

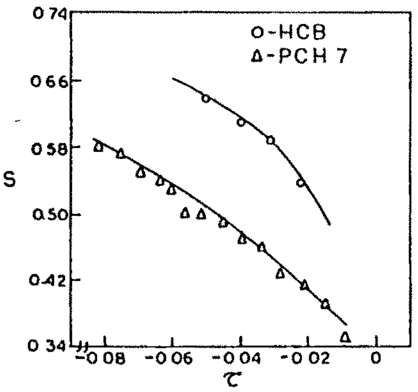


FIGURE 3b Plots of order parameter S vs τ for HCB and PCH-7

the PCH liquid crystals. These results are in agreement with the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ reported earlier for alkyl cyanobiphenyl,[10] P-alkoxybenzilidiene, P-aminobenzonitriles[11] which have got strong dipole moment. For liquid crystals, having small and zero dipole moment it was shown by de Jeu et al.[12] that $\bar{\epsilon}$ coincides with dielectric constant ϵ_{is} at the clearing temperature.

From these results it appears that though Maier and Meiers' theory gives qualitatively correct representation of dielectric properties in nematic liquids having small or zero dipole moment, it fails to do so in the case of strongly polar liquid crystals.

From Table V is can be seen that the experimental values of $\epsilon_{\parallel}$ is nearly half of the values of $\epsilon_{\parallel}$, calculated from Maier and Meiers' equation (1) using Polarizability α and order parameter S obtained from refractive index measurements. Similarly the value of the order parameter S calculated from experimental values of dielectric anisotropy $\Delta\epsilon$, using Maier and Meier equation (3) comes out much less than that obtained from birefringence or other methods. Similar results were also reported earlier in the case of cyanobiphenyls,

TABLE V

Comparison of $\epsilon_{\parallel}$ values obtained experimentally with $\epsilon_{\parallel}$ values calculated from birefringence data

7 ^{0}C	Expt $\epsilon_{\parallel}$ values	$\epsilon_{\parallel}$ values calculated from birefringence data
PCH-3 43	16 58	38 60
PCH-5 33	14 74	26 80
PCH-7 31	12 85	23 10

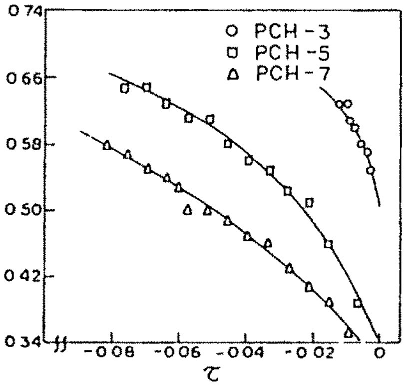


FIGURE 4 Order parameter S vs τ for PCH-3, PCH-5, PCH-7

cyanophenylheptylbenzoate[5] Thus the results show that Maier and Meiers' theory for dielectric constants in anisotropic media of strongly polar molecules fails to give consistent results with the experimental values This is due to the fact that only long range order was considered in Maier and Meiers's theory, existence of short range order was completely ignored. Madhusudan and Chandrasekhar[13] in their theory proposed the existence of antiferroelectric short range order in nematic phase of strongly polar molecules. Such short range antiparallel ordering in strongly polar nematic liquid crystals might cause a large decrease in $\epsilon_{\parallel}$, resulting in a decrease in dielectric anisotropy $\Delta\epsilon$ and thus a decrease on order parameter.

Acknowledgement

We thank Prof G S Kastha for his interest

References

1 S Sen, P Brahma, S K Roy, D K Mukherjee and S B Roy, *Mol Cryst Liq Cryst* **100**, 327 (1983)
2 H E J Neugebauer *Canad J Phys* **18** 292 (1950)
3 M F Vuks *Optics and Spectroscopy* **20** 361 (1966)
4 A Saupe and W Maier, *Z Natur-forschg* **16a** 816 (1961)
5 S Sen, P Brahma S K Roy and S B Roy, *Acta Phys Polonica* (Dec 1983)
6 I Haller, H A Higgins, H R Lilienthal and T R McGuire *J Phys Chem* **77**, 950 (1973)
7 W Maier and G Meier, *Z Naturforschug* **16a** 262 (1961)
8 I H Ibrahim and W Haase *Mol Cryst Liq Cryst* **66**, 189 (1981)

9 L Pohl, R Eidenschink, G Krause and D Erdmann, *Phys Letters* **60A**, 421 (1977)
10 S Sen and S K Roy, *Proceed of the 71st Indian Sc Congress*
11 M Schadt, *J Chem Phys* **56** 1994 (1972)
12 W H de Jeu and Th W Lathouwers *Z Naturforschg* **29a**, 905 (1974)
13 N V Madhusudana and S Chandrasekhar, *Proc International Conf on Liquid Crystals*, Bangalore 1973, p 427

Refractive Indices, Dielectric Constants, and Order Parameter of Four Alkyl/Alkoxyphenylcyclohexanecarboxylate Liquid Crystals in the Nematic Phase

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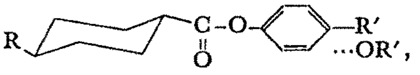
The extraordinary and ordinary refractive indices, n_e and n_o, and the densities of four liquid crystals 4-pentylphenyl *trans*-4′-pentylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4′-propylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4′-butylcyclohexanecarboxylate, and 4-methoxyphenyl *trans*-4′-pentylcyclohexanecarboxylate have been reported at different temperatures. The effective polarizabilities α_e and α_o in the nematic phase have been calculated using 1) Neugebauer and 2) Vuks methods The order parameter S calculated from the two methods were comparable The dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$, parallel and perpendicular to the long axis of the molecules have been measured at 1 kHz at different temperatures. The order parameters for the liquid crystals were then evaluated from dielectric anisotropy $\Delta\varepsilon(=\varepsilon_\parallel-\varepsilon_\perp)$, polarizability anisotropy $\Delta\alpha(=\alpha_e-\alpha_o)$ and dipole moment μ, using Maier and Meier equation and were found only slightly less than those obtained from refractive indices method. It was concluded that Maier and Meier equation also could be used to evaluate the order parameter of liquid crystals of molecules having dipole moments 2 Debye or less.

The knowledge of dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$, parallel and perpendicular to the long molecular axis helps us to select a liquid crystal for a specific electrooptical display device. The values of dielectric anisotropy $\Delta\varepsilon(=\varepsilon_\parallel-\varepsilon_\perp)$ and polarizability anisotropy $\Delta\alpha(=\alpha_e-\alpha_o)$ where α_e and α_o are the effective polarizabilities of the nematic medium and the dipole moment μ may be useful for the evaluation of order parameter of liquid crystals using Maier and Meier equation.[1] de Jeu and Lathouwers[2,3] observed that in the case of liquid crystals with zero or small dipole moment, the average dielectric constant $\bar{\varepsilon}=1/3\,(\varepsilon_\parallel+2\varepsilon_\perp)$ practically coincides with the dielectric constant $\varepsilon_{\rm iso}$ in the isotropic phase They pointed out that these results indicate that the Maier and Meier equation gives qualitatively the correct picture of dielectric properties of liquid crystals. But for the lack of information on molecular polarizabilities, dipole moments, and their angle with the long molecular axis, the model could not be tested for quantitative measurements. Recently Sen *et al.*[4] observed that in the case of liquid crystals of strongly polar molecules having dipole moments of 4—5 Debye,† the order parameter S obtained from Maier and Meier equation using dielectric anisotropy and polarizability anisotropy are much less than the values obtained from other methods Sen *et al* [4] pointed out that the short range antiferroelectric dipole correlation of permament dipole moment μ in strongly polar nematics as proposed by Madhusudana and Chandrasekhar[5] might cause a large decrease in $\varepsilon_\parallel$ thus decreasing the order parameter. The object of the present investigation is to evaluate the order parameter S of liquid crystals with dipole moments about 2 Debye from the measurements of refractive indices and densities, and to compare these S values with those obtained from dielectric anisotropy $\Delta\varepsilon$ and polarizability anisotropy $\Delta\alpha$, using the Maier and Meier equation.[1]

Experimental

The structural formulae and nematic-isotropic transition temperatures of four liquid crystals which were obtained from Merck are given below The general formula for these compounds is



where R and R′=Alkyl and OR′=Alkoxy.

1) 4-Pentylphenyl *trans*-4′-pentylcyclohexanecarboxylate (D-55)

$$C \xrightarrow{37\,^\circ\mathrm{C}} N \xrightarrow{47\,^\circ\mathrm{C}} I$$

2) 4-Ethoxyphenyl *trans*-4′-propylcyclohexanecarboxylate (D-302)

$$C \xrightarrow{48\,^\circ\mathrm{C}} N \xrightarrow{78\,^\circ\mathrm{C}} I$$

3) 4-Ethoxyphenyl *trans*-4′-butylcyclohexanecarboxylate (D-402)

$$C \xrightarrow{37\,^\circ\mathrm{C}} N \xrightarrow{75\,^\circ\mathrm{C}} I$$

4) 4-Methoxyphenyl *trans*-4′-pentylcyclohexanecarboxylate (D-501)

$$C \xrightarrow{40\,^\circ\mathrm{C}} N \xrightarrow{71\,^\circ\mathrm{C}} I$$

The liquid crystals were used in the investigations without further purification.

Measurement of Refractive Indices The refractive indices n_o and n_e for the ordinary and extraordinary refracted rays in the nematic phase and the refractive index n in the isotropic phase at different temperatures were measured by means of an Abbe refractometer. The glass prisms of the refractometer were first treated with an aqueous solution of 3% poly (vinyl alcohol) and dried The prism was then rubbed with a lens paper along the length of prism several times A little of the liquid crystal was dropped on the lower prism

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† $1\,\mathrm{D}=3\ 3\times10^{-30}$cm.

and was spread with a spatula. These operations helped to align the liquid crystal along the length of the prism surface. The arrangement was complete when the upper prism was clamped in place.

Two positions of a nicol placed over the eyepiece allow distinct separation of bright and dark space corresponding to n_e and n_o (in the nematic $n_e>n_o$). The temperature was maintained constant within ±0.2°C by means of a thermostat.

The densities of the liquid crystal in the nematic and isotropic phases were determined by introducing a weighed sample of the liquid crystal into a capillary tube placed in a thermostat. The length of the column in the capillary was measured at different temperatures with a travelling microscope. The density was calculated after correcting for the expansion of the glass tube.

Measurements of Dielectric Constants $\varepsilon_\parallel$ and $\varepsilon_\perp$. The static dielectric constants were measured at a frequency of 1 kHz using a GR-1620 capacitance bridge reading to an accuracy of 0.01%. A parallel plate capacitor with stainless steel electrodes of 2 cm×1 cm separated by a 1 mm teflon spacer, served as the sample holder. The temperature of the sample was measured with a thermocouple mounted directly on one of the electrodes. A magnetic field 1.0 T was used to align the liquid crystal molecules parallel and perpendicular to the electrode surfaces. The temperature of the sample holder was maintained constant within ±0.2 °C by means of a thermostat. The cell was calibrated with freshly distilled toluene and chlorobenzene and the values agree to 0.1% of the standard value.[6]

Results

Refractive Indices and Polarizabilities. The experimental values of refractive indices n_e, n_o, and n and the densities of the liquid crystals are given in Tables 1 (a, b, c, d) and Fig. 1. The effective polarizabilities α_e and α_o in the nematic state were calculated using two methods. 1) Neugebauer's[7] method of anisotropic internal field given by

$$n_{e,o}^2 - 1 = 4\pi N\alpha_{e,o}/(1-N\alpha_{e,o}\text{-}\gamma_{e,o}), \tag{1}$$

where N is the number of molecules per 1 cm³ and $\gamma_{e,o}$ are internal field constants. The relevant equations for calculating the polarizabilities are

$$\frac{1}{\alpha_e}+\frac{2}{\alpha_o}=\frac{4\pi N}{3}\left[\frac{n_e^2+2}{n_e^2-1}+\frac{2(n_o^2+2)}{(n_o^2-1)}\right], \tag{2}$$

$$\alpha_e+2\alpha_o=\alpha_{//}+2\alpha_\perp=\frac{9}{4\pi N}\left(\frac{n^2-1}{n^2+2}\right). \tag{3}$$

Table 1a Refractive indices, density and order parameter S for D-55

T/°C	n_o	n_e	ρ/g cm^{-3}	$\bar{\alpha}$/Å^3	Vuks' Method			Neugebauer's Method		
					α_o/Å^3	α_e/Å^3	S	α_o/Å^3	α_e/Å^3	S
36	1.4730	1.5304	0.9508	41.632	39.683	45.532	.70	39.995	44.908	.69
37	1.4724	1.5301	0.9501	41.623	39.664	45.550	.70	39.989	44.900	.69
39	1.4724	1.5272	0.9468	41.623	39.757	45.357	.67	40.058	44.753	.66
41	1.4720	1.5250	0.9486	41.629	39.818	45.241	.65	40.090	44.708	.65
43	1.4722	1.5217	0.9449	41.643	39.867	45.020	.61	40.206	44.518	.60
45	1.4736	1.5163	0.9431	41.652	40.190	44.571	.52	40.413	44.132	.52
47	1.4870		0.9416							
48.5	1.4862		0.9389							
51.5	1.4848		0.9357							
					$\alpha_\perp=$ 38.869 (Å)^3	$\alpha_\parallel=$ 47.2717 (Å)^3		$\alpha_\perp=$ 39.310 (Å)^3	$\alpha_\parallel=$ 46.398 (Å)^3	

Table 1b Refractive indices, density and order parameter S for D-302

T/°C	n_o	n_e	ρ/g cm^{-3}	$\bar{\alpha}$/Å^3	Vuks' Method			Neugebauer's Method		
					α_o/Å^3	α_e/Å^3	S	α_o/Å^3	α_e/Å^3	S
51	1.4705	1.5448	1.0118	33.1706	31.1645	37.1733	.75	31.4817	36.5486	.75
54.5	1.4700	1.5417	1.0093	33.1730	31.2352	37.0442	.72	31.5438	36.4314	.72
57	1.4693	1.5401	1.0074	33.1790	31.2605	37.0092	.71	31.5646	36.4078	.71
60	1.4684	1.5384	1.0048	33.1960	31.2950	36.9931	.71	31.5954	36.3972	.71
63	1.4680	1.5356	1.0024	33.2063	31.3670	36.8800	.69	31.6581	36.3028	.69
66	1.4677	1.5327	1.0000	33.2183	31.4441	36.7570	.66	31.7181	36.2188	.66
69	1.4677	1.5289	0.9974	33.2293	31.5552	36.5697	.62	31.8137	36.0606	.63
72	1.4674	1.5263	0.9947	33.2550	31.6408	36.4781	.60	31.8919	35.9812	.61
75	1.4677	1.5222	0.9921	33.2713	31.7757	36.2608	.56	32.0104	35.7932	.56
77	1.4680	1.5198	0.9900	33.2956	31.8844	36.1550	.53	32.1633	35.5604	.50
78	1.4698	1.5146	0.9888	33.3126	32.0789	35.7753	.46	32.2666	35.4048	.46
79	1.4845		0.9849							
80	1.4842		0.9841							
84.5	1.4824		0.9804							
88	1.4810		0.9776							
					$\alpha_\perp=$ 30.7379 (Å)^3	$\alpha_\parallel=$ 38.7851 (Å)^3		$\alpha_\perp=$ 31.1611 (Å)^3	$\alpha_\parallel=$ 37.9387 (Å)^3	

Table 1c Refractive indices, density and order parameter S for D-402

$T/°C$	n_o	n_e	$\rho/g\,cm^{-3}$	$\bar{\alpha}/Å^3$	Vuks' Method			Neugebauer's Method		
					$\alpha_o/Å^3$	$\alpha_e/Å^3$	S	$\alpha_o/Å^3$	$\alpha_e/Å^3$	S
40	1 4730	1 5508	1 0106	35 0349	32 8309	39 4324	73	33 1803	38 7443	73
44	1 4723	1 5469	1 0072	35 0449	32 9238	39 2740	70	33 2561	38 6227	70
45 5	1 4712	1 5473	1 0063	35.0406	32 8772	39 3628	72	33 2233	38 6752	71
52	1 4703	1 5408	1 0012	35 0499	33 0334	39 0702	67	33 3455	38 4589	67
55 5	1 4695	1 5380	0 9986	35 0513	33 0898	38 9691	65	33 4004	38 3531	65
59 5	1 4686	1 5345	0 9958	35 0389	33 1471	38 8183	63	33 4507	38 2154	62
64	1.4685	1 5288	0 9923	35 0433	33 3030	38 5099	.57	33 5646	38 0007	58
67	1 4682	1 5256	0 9897	35 0539	33 3974	38 3626	.55	33 6578	37 8462	55
69	1 4680	1 5234	0 9879	35 0629	33 4629	38 2637	53	33 7192	37 7505	53
71	1 4680	1 5207	0 9860	35 0756	33 5470	38 1216	50	33 7745	37 6779	51
73	1 4690	1.5164	0 9841	35 0939	33 7161	37 8363	45	33 9132	37 4554	46
74	1 4698	1 5137	0 9832	35 1016	33 5238	37 6430	45	34.0195	37 2659	42
75 5	1 4840		0 9815							
76 5	1 4835		0 9791							
78	1 4828		0 9778							
80	1 4820		0 9761							
					$\alpha_\perp=$ 32 1041 (Å)^3	$\alpha_\parallel=$ 41 1670 (Å)^3		$\alpha_\perp=$ 32 5785 (Å)^3	$\alpha_\parallel=$ 40 2182 (Å)^3	

Table 1d Refractive indices, density and order parameter S for D-501

$T/°C$	n_o	n_e	$\rho/g\,cm^{-3}$	$\bar{\alpha}/Å^3$	Vuks' Method			Neugebauer's Method		
					$\alpha_o/Å^3$	$\alpha_e/Å^3$	S	$\alpha_o/Å^3$	$\alpha_e/Å^3$	S
40	1 4772	1 5445	1 0164	34 870	32 975	38 646	73	33 270	38 070	73
50	1 4742	1 5389	1 0087	34 900	33 065	38 561	71	33 355	37 990	71
60 5	1 4725	1 5302	1 0068	34 720	33 084	37 993	63	33 354	37 452	63
65	1 4723	1 5256	0 9970	34 956	33 430	38 005	59	33 665	37 540	59
70	1 4732	1 5180	0 9924	34 996	33 710	37 570	50	33 921	37 148	49
72 5	1 4752	1 5112	0 9896	35 033	34 000	37 107	40	34 186	36 728	39
74 5	1 4865		0 9861							
75 5	1 4860		0 9854							
					$\alpha_\perp=$ 32 533 (Å)^3	$\alpha_\parallel=$ 40 283 (Å)^3		$\alpha_\perp=$ 32 936 (Å)^3	$\alpha_\parallel=$ 39 477 (Å)^3	

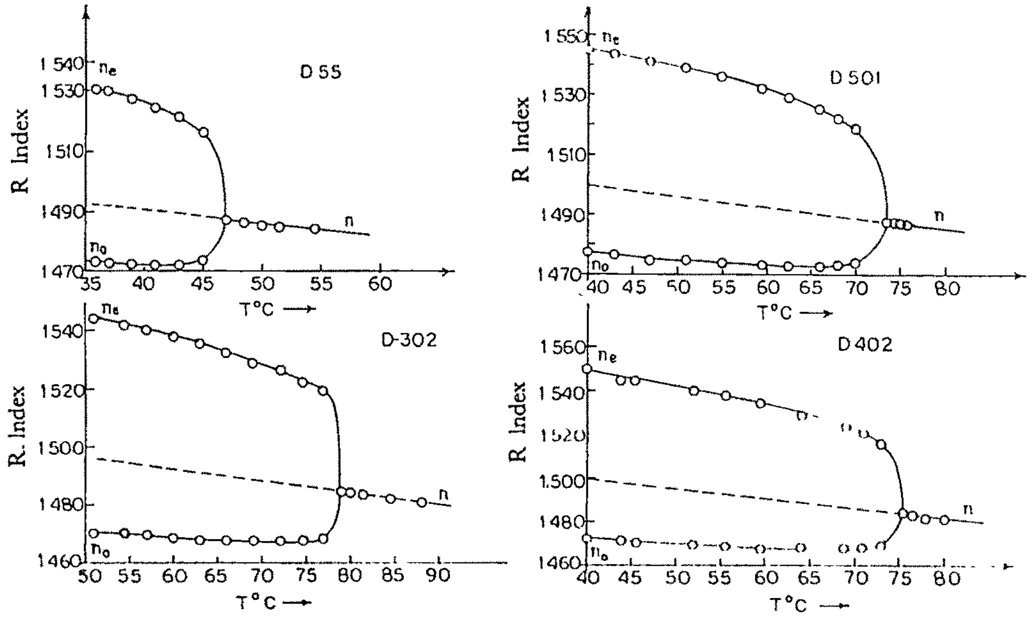

Fig 1 Refractive index anisotropy plots for D-55, D-501, D-302, and D-402

2) Vuks'method[8] of isotropic internal field given by

$$\frac{n_{e,o}^2-1}{\overline{n^2}+2}=\frac{4\pi N\alpha_{e,o}}{3}, \tag{4}$$

where $\overline{n^2}=1/3\ (n_e^2+2n_o^2)$

The values of effective polarizabilities α_e and α_o obtained from the two methods are included in Tables 1 (a, b, c, d) Since the principal polarizabilities $\alpha_\parallel$ and $\alpha_\perp$, parallel and perpendicular to the long axis of the molecules in the crystalline state, were not available, the method of Haller *et al* [9] was adopted Graphs were plotted with log α_e/α_o *vs.* log (T_c-T) where T_c is the nematic-isotropic transition temperature These plots are straight lines at lower temperatures and intersect the log α_e/α_o axis at 0 K assumed to correspond to log $\alpha_\parallel/\alpha_\perp$ in the crystalline state From Eq 3 the values of $\alpha_\parallel$ and $\alpha_\perp$ are obtained The order parameter S was then calculated from the relation $S=\alpha_e-\alpha_o/\alpha_\parallel-\alpha_\perp$.

Dielectric Constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ and the Order Parameter. The experimental values of dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ of the liquid crystals in nematic state and that in the isotropic phase ε_{iso} are given in Table 2 The dielectric anisotropy is shown in Fig 2 The order parameter was calculated using the Maier and Meier equation,[1]

$$\Delta\varepsilon = 4\pi NhF\left[\Delta\alpha-\frac{F\mu^2}{2kT}(1-3\cos^2\beta)\right]S, \tag{5}$$

where N is the number of molecules per 1 cm³, $h=3\bar{\varepsilon}/(2\bar{\varepsilon}+1)$, the cavity field factor, $F=1/(1-\bar{\alpha}f)$, the reaction field factor, and $f=4\pi N(2\bar{\varepsilon}-2)/3(2\bar{\varepsilon}+1)$, μ the dipole moment of the molecule, $\Delta\alpha$=polarizability anisotropy $=\alpha_e-\alpha_o$, and $\Delta\varepsilon=\varepsilon_\parallel-\varepsilon_\perp$ dielectric anisotropy.

The dipole moments μ of the liquid crystal molecules were determined in dilute solutions in benzene and included in Table 2. The angle between the resultant moment and the long axis of the molecules of the liquid crystals (β) was calculated from the alkoxyl

TABLE 2 VALUES OF DIELECTRIC PERMITTIVITIES $\varepsilon_\parallel$, $\varepsilon_\perp$, AND ε_{iso}

D-55			D-302			D-402			D-501		
T/°C	$\varepsilon_\parallel$	$\varepsilon_\perp$	T/°C	$\varepsilon_\parallel$	$\varepsilon_\perp$	T/°C	$\varepsilon_\parallel$	$\varepsilon_\perp$	T/°C	$\varepsilon_\parallel$	$\varepsilon_\perp$
37.5	2.940	3.419	51	3.2816	4.5447	40	3.2720	4.4947	43	3.4125	4.4595
40	2.958	3.396	54.5	3.2798	4.5150	52	3.2355	4.3607	47	3.3583	4.4137
42	2.958	3.382	60	3.2952	4.4732	59.5	3.2483	4.2246	51	3.3685	4.2837
44	2.984	3.351	66	3.3024	4.4155	69	3.3229	4.0941	55	3.3182	4.2423
46	2.997	3.313	72	3.3369	4.2613	73	3.3572	4.0179	60.5	3.3372	4.1875
50 iso	3.226		77	3.3566	4.1899	77 iso	3.7435		65	3.3560	4.1244
52	3.217		80	3.4673	4.0482	80	3.7143		70	3.4083	3.9952
54	3.208		84.5 iso	3.8518		85	3.6798		74 iso	3.8101	
			88	3.8308		88	3.6548		76	3.7936	
			90	3.8208					78	3.7727	
									80	3.7563	
									85	3.7110	
μ=1.99 D, β=66°			μ=2.17 D, β=72°			μ=2.08 D, β=72°			μ=2.23 D, β=68°		

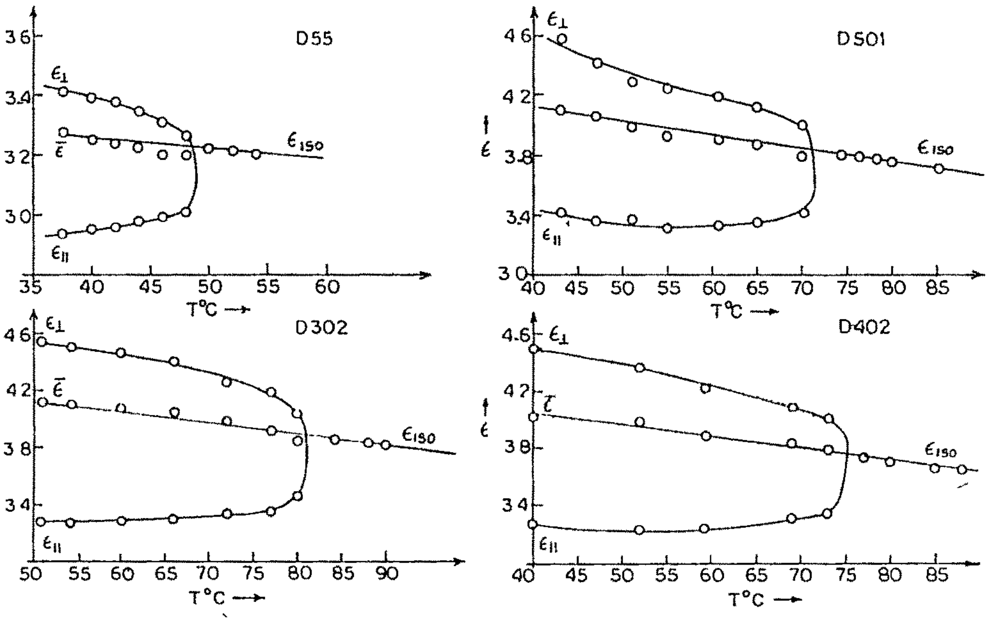

Fig 2 Dielectric anisotropy plots for D-55, D-501, D-302, and D-402

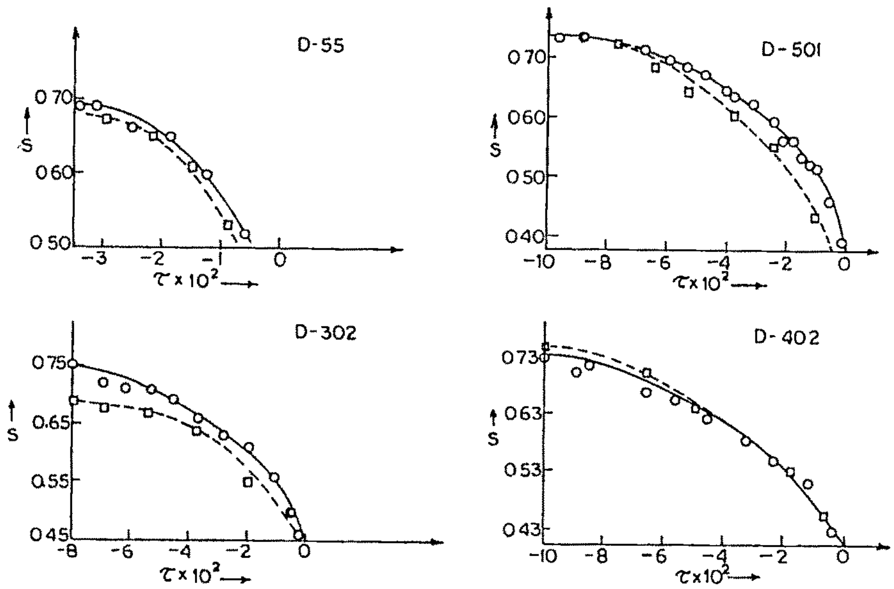

Fig. 3. Plots of order parameter S *vs* $\tau=(T-T_{NI})/T_{NI}$.
By ○—Neugebauer's method, and □—Maier and Meier's method.

group moment and ester group moment reported in the literature.[10] The angle β for the different samples is given in Table 2

Discussion

It can be seen from Tables 1 (a, b, c, d) that the order parameters S for the liquid crystals under study, obtained from the refractive indices using 1) Neugebauer and 2) Vuks methods are comparable. The S value decreases with increase of temperature till it suddenly vanishes at the clearing temperature The order parameters for these liquid crystals have not been reported so far

From Fig 2, it can be seen that the average dielectric constants $\bar{\varepsilon}=(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3$ in the nematic phase practically coincide with the dielectric constants ε_{iso} in the isotropic phase. These results are similar to those reported by de Jeu[3] in the case of liquid crystals of very small or zero dipole moment but unlike to the case of liquid crystals having large dipole moment (μ=4—5 Debye) of which the average dielectric constant ε_{iso} in the isotropic phase reported by different workers [11,12]

From Table 2, it can be seen that the values of the order parameter S, calculated from the values of the dielectric anisotropy $\Delta\varepsilon$, polarizability anisotropy $\Delta\alpha$ and dipole moment μ using the Maier and Meier equation for the alkoxyphenyl *trans*-4′-alkylcyclohexanecarboxylates, compare very well at all temperatures with those obtained from refractive index methods Similarly for alkylphenyl *trans*-4′-alkylcyclohexanecarboxylates, the order parameters S from the Maier and Meier equation also agree well with those obtained from the refractive index methods, though the former values are only slightly less than the latter. The slight discrepancy may be due to the estimation of the angle β made by the resultant moment with the long of the molecule So, it appears that for liquid c tals having dipole moment of about 2D, or so, Maier and Meier equation with dielectric aniso $\Delta\varepsilon$, provides another method for the determina of the order parameter.

The inapplicability of the Maier and Meier the for dielectric constants in strongly polar nem might be due to short range antiferroelectric di correlation of the permanent dipole moment as posed by Madhusudana and Chandrasekhar,[5] wl might cause a large decrease in $\varepsilon_{\parallel}$ in strongly p nematics (μ>4 D); Such a decrease in $\varepsilon_{\parallel}$ in less p nematics ($\mu\approx$2D) might not affect the dielectric isotropy and hence the order parameter very e tively.

Of course some more liquid crystals having ments of more or less 2D should be studied be drawing definite conclutions

Our sincere thanks to Dr S B Roy for his guida

References

1) W Maier and G Meier, *Z Naturforsch*, *A*, **16**, (1961)

2) W H de Jeu and Th W Lathouwers, *Z Naturfors* *A*, **29**, 905 (1974)

3) W H. de Jeu and Th. W. Lathouwers, *Z. Naturfors* *A*, **30**, 79 (1975).

4) S Sen, P Brahma, S K Roy, and S B Roy, *Acta P* *Pol*, *A*, **65**, 47 (1984)

5) N V. Madhusudana and S Chandrasekhar, P International Conf. on Liquid Crystals, Bangalore (1973 427

6) C D Hodgman, R. C. Weast, R S Shanklend, S M Selby, "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co, Cleveland, Ohio (19

pp 2556—2557

7) H E J. Neugebauer, *Can. J Phys.*, **32**, 1 (1954).

8) M F. Vuks, *Opt Spektrosk*, **20**, 361 (1966)

9) I Haller, H A Huggins, H R Lilienthal, and T. R. McGuire, *J Phys Chem*, **77**, 950 (1973).

10) V. I. Minkin, O. A. Osipov, and Y. A. Zhadanov, "Dipole Moments in Organic Chemistry," Plenum Press, NY-London (1970), p 91.

11) M Schadt, *J. Chem Phys*, **56**, 1494 (1972)

12) B. R Ratna and R. Sashidhar, *Pramana*, **6**, 278 (1976)

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DIELECTRIC PERMITTIVITIES AND REFRACTIVE INDICES STUDIES IN SOME MONOTROPIC AND THERMOTROPIC LIQUID CRYSTALS

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Studies on dielectric permittivities $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and extraordinary and ordinary refractive indices n_e, n_0 for two monotropic liquid crystals: *p*-cyanophenyl-*p'*-butyl benzoate (CPBB) and *p*-cyanophenyl-*p'*-pentyloxy benzoate (CPPOB) and one thermotropic liquid crystal mixture E_4 have been reported. The orientational order parameter for all the liquid crystals evaluated from refractive indices using 1) Neugebauer and 2) Vuks methods are in good agreement. The order parameter evaluated from dielectric anisotropy $\Delta\varepsilon$ using Maier and Meier's equation are found to be much smaller than those obtained from refractive indices and in agreement with the results in strongly polar nematics reported earlier. The pretransitional effect for dielectric permittivity $\varepsilon_{\mathrm{iso}}$ in isotropic phase, showing a maximum in $\varepsilon_{\mathrm{iso}}$ a little above T_{NI} has been observed in all the liquid crystals. The results have been discussed.

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1. Introduction

Studies on dielectric properties and refractive indices on thermotropic liquid crystals have been reported by different workers [1-6]. But such studies on monotropic liquid crystals are very scarce. The object of the present investigation was to study how the long range order parameter of these liquid crystals evaluated from refractive indices conform to those obtained from dielectric constants using Maier and Meier equation [7].

It is now well known that at the nematic-isotropic phase transition the long range nematic ordering vanishes, but short range ordering still persists well into isotropic phase influencing some physical properties such as magnetic birefringence, Kerr constant, light scattering, dielectric permittivity etc. just near the transition temperature. We shall report our observations of such pretransition effect in dielectric permittivity of two monotropic liquid crystals CPBB and CPPOB and one thermotropic liquid crystal E_4. The results will be discussed in the paper.

2. *Experimental*

The liquid crystals studied here are:

1) p-cyanophenyl p'-butyl benzoate (CPBB) — mesomorphic range 52°–54°C, 43°C monotropic nematic
2) p-cyanophenyl p'-pentyloxy benzoate (CPPOB) — mesomorphic range 82°C–84°C, 76.5°C monotropic nematic
3) E_4 mixture of 7CB, 5-OCB, 7-OCB, 8-OCB in the proportion of 44, 19, 16 and 21 respectively. Nematic range: 4°C to 61°C

The monotropic liquid crystals CPBB and CPPOB were obtained from Eastman Kodak and the mixture E_4, B.D.H. England. The liquid crystals were used in the investigations without further purification.

Measurement of refractive indices

The refractive indices n_e and n_0 for the extraordinary and ordinary rays in the nematic phase and the refractive index n in the isotropic phase at different temperatures were measured by means of an Abbe refractometer. The method of aligning the liquid crystals and measuring the refractive indices were described earlier [6].

The density of a liquid crystal in the nematic and isotropic phase at different temperatures were determined by introducing a weighed sample of the liquid crystal into a capillary tube placed in a thermostat. The length of the column in the capillary was measured at different temperatures with a travelling microscope. The density was calculated after correcting for the expansion of the glass tube.

Measurement of dielectric permittivities

The static permittivities were measured at a frequency of 1 KHz using a GR — 1620 capacitance bridge reading to an accuracy of 0.01 %. A parallel plate capacitor with stainless steel electrodes of 2.5 cm diameter separated by 1 mm teflon spacer served as the sample holder. The temperature of the sample was measured with a thermocouple attached to one of the electrodes. A magnetic field of 1 T was used to align the liquid crystal molecules parallel and perpendicular to the electrode surfaces. The temperature of the sample was maintained constant by means of a thermostat. The cell was calibrated with freshly distilled toluene and chlorobenzene and the values of dielectric permittivities agree to 0.01 % of the standard value.

3. *Results*

The experimental values of the refractive indices n_e, n_0 and the densities ϱ of the liquid crystals are given in Table I. The effective polarizabilities α_e and α_0 shown in Fig. 1a, b, c in the nematic phase were calculated using 1) Neugebauer's [8] and 2) Vuks methods [9] as described earlier [5, 6]. The principal polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ parallel and perpendicular to the long axis of the molecules in the crystalline phase were evaluated using the method due to Haller et al. [10]. The order parameter was calculated from the relation

$$S = \frac{\alpha_e - \alpha_0}{\alpha_{\parallel} - \alpha_{\perp}}.$$

TABLE I

Refractive indices and densities of CPBB, CPPOB and Mixture E_4

CPBB				CPPOB				Mixture E_4			
Temp. [°C]	n_o	n_e	ϱ [g/cm³]	Temp. [°C]	n_o	n_e	ϱ [g/cm³]	Temp. [°C]	n_o	n_e	ϱ [g/cm]³
80	1.5476		1.061	88.5	1.5450		1.073	38	1.5162	1.6993	1.022
74.5	1.5492		1.065	85.5	1.5460		1.075	43	1.5174	1.6899	1.018
69	1.5514		1.070	82.5	1.5475		1.078	47	1.5182	1.6829	1.014
60.5	1.5548		1.076	79.5 Iso	1.5486		1.080	50	1.5190	1.6758	1.011
56	1.5572		1.081	74	1.5123	1.6256	1.083	53	1.5202	1.6708	1.008
50	1.5594		1.084	72	1.5105	1.6309	1.090	56	1.5228	1.6618	1.005
45	1.5614		1.088	69	1.5082	1.6389	1.093	59	1.5272	1.6486	1.003
43 Iso	1.5624		1.089	65.5	1.5070	1.6482	1.096	62 Iso	1.5675		0.997
41	1.5290	1.6294	1.095	62.5	1.5065	1.6505	1.099	63	1.5672		0.996
40	1.5266	1.6348	1.095	59	1.5060	1.6565	1.102	65	1.5656		0.994
39	1.5250	1.6392	1.096	55.5	1.5055	1.6599	1.106	68	1.5640		0.992
38	1.5238	1.6423	1.097	52.5	1.5048	1.6649	1.109	71	1.5634		0.989
37	1.5230	1.6449	1.098	49	1.5040	1.6708	1.112				
36	1.5222	1.6476	1.099								
35	1.5214	1.6505	1.100								

Values of $\alpha_\perp$ and $\alpha_\parallel$ obtained for Vuks and Neugebauer's methods for (1) CPBB, (2) CPPOB and (3) Mixture E_4 are:

(1) 27.964 (Å)^3, 42.855 (Å)^3 and 28.809 (Å)^3, 41.165 (Å)^3

(2) 29.677 (Å)^3, 48.801 (Å)^3 and 30.661 (Å)^3, 46.838 (Å)^3

(3) 29.492 (Å)^3, 51.605 (Å)^3 and 30.817 (Å)^3, 48.954 (Å)^3 respectively.

The experimental values of dielectric permittivity $\varepsilon_\parallel$ and $\varepsilon_\perp$ in the nematic and ε_{iso} in the isotropic phase, Table II are shown in Fig. 2a, b, c. The dipole moments μ of the liquid crystals were determined in dilute solution in benzene [15].

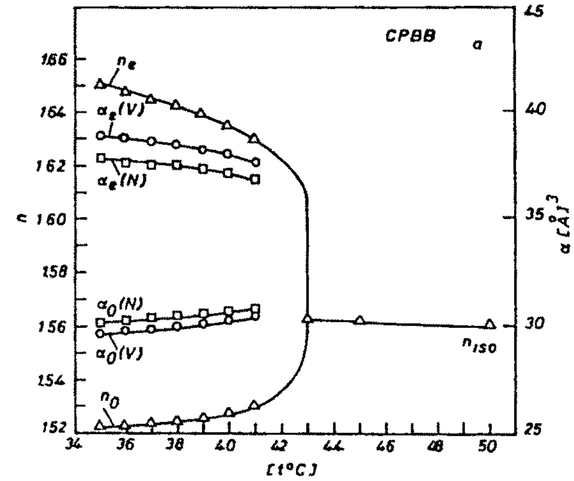

Fig. 1a

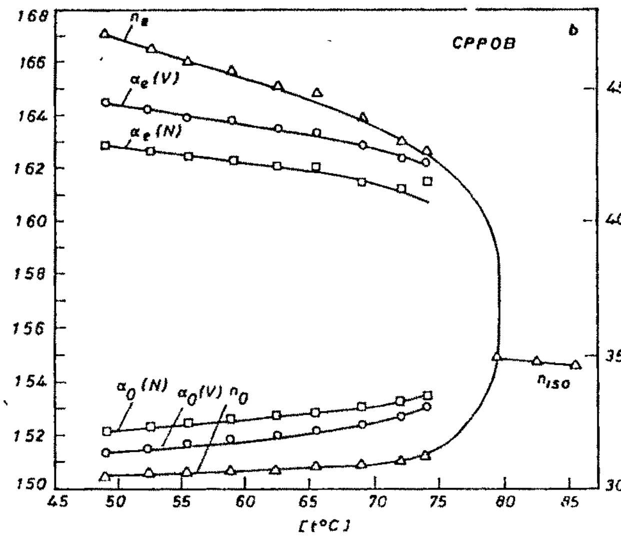

Fig 1b

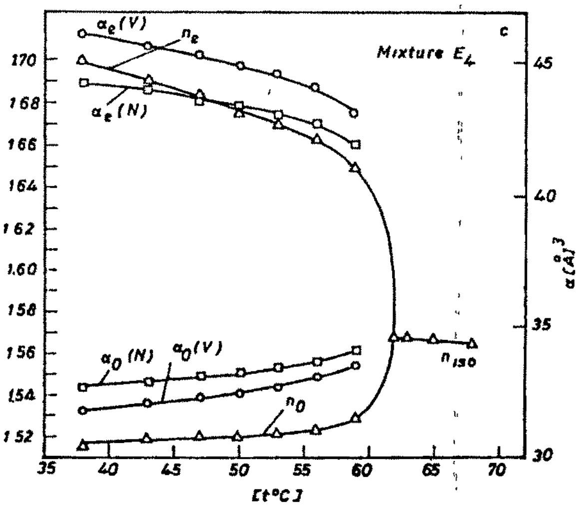

Fig. 1c

Fig. 1a, b, c. Plots of refractive indices n_e, n_0 and n and polarizabilities $\alpha_e(V)$, $\alpha_0(V)$, $\alpha_e(N)$, $\alpha_0(N)$ vs temperature where (V) stands for Vuks' method and (N) stands for Neugebauer's method

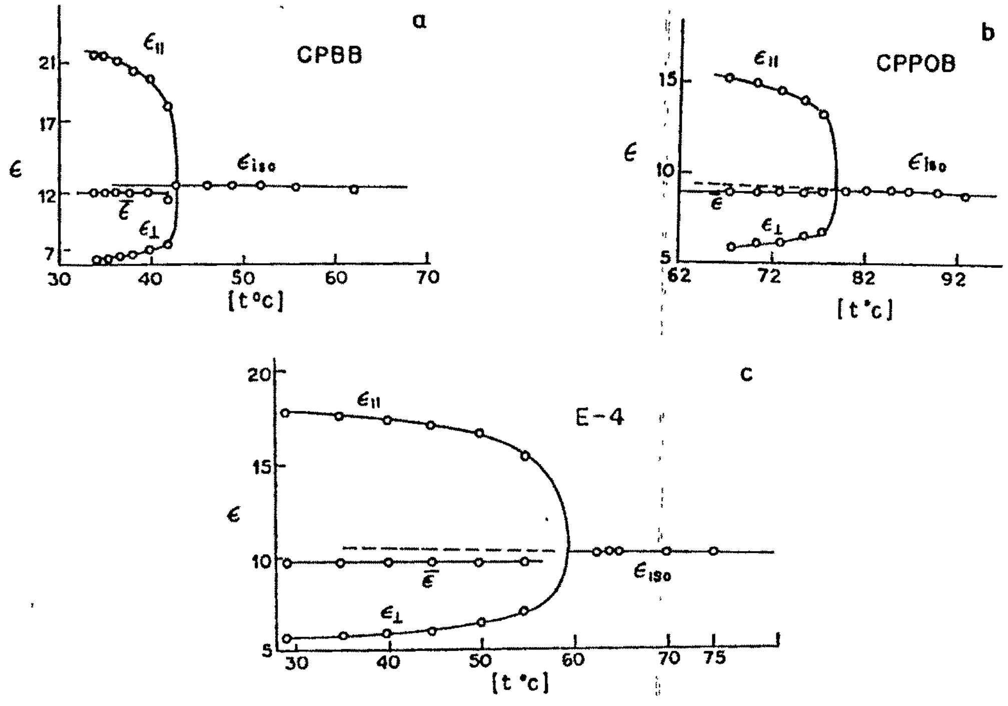

Fig. 2a, b, c. Plots of dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ vs temperature

TABLE II

Values of the dielectric permittivities $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_{iso} of CPBB, CPPOB, Mixture E_4

CPBB ($\beta = 25°$)				CPPOB ($\beta = 30°$)				Mixture E_4 ($\beta = 0°$)			
Temp. [°C]	$\varepsilon_{\parallel}$	ε_{iso}	$\varepsilon_{\perp}$	Temp [°C]	$\varepsilon_{\parallel}$	ε_{iso}	$\varepsilon_{\perp}$	Temp. [°C]	$\varepsilon_{\parallel}$	ε_{iso}	$\varepsilon_{\perp}$
62		12.234		93		8.843		29	17.867		5.708
56		12.398		90		8.897		35	17.704		5.824
52		12.540		87		9.100		40	17.490		5.947
49		12.561		85		9.150		45	17.042		6.138
46		12.582		82.5		9.168		50	16.552		6.454
43 Iso		12.512		80 Iso		9.088		55	15.275		6.895
42	17.933		8.434	77.5	13.319		6.692	62.5 Iso		10.352	
40	19 947		8.048	75.5	13.961		6.410	64		10.401	
38	20.689		7.743	73	14.536		6.215	65		10.352	
36.5	21.035		7.680	70.5	14 964		6.053	70		10.292	
35	21.552		7.594	67.5	15.344		5.811	75		10.119	
34	21.547		7.427								

4. *Discussion*

It can be seen from the Table III that the orientation order parameter of the monotropic liquid crystals CPBB and CPPOB obtained from the refractive indices using 1) Neugebauer's and 2) Vuks methods are in good agreement at all temperatures. The orientational order increases with decrease of temperature and at the clearing temperature, it vanishes. In the case of the thermotropic liquid crystal E_4 the order parameters by different methods are also comparable and with the increase of temperature it decreases, Table III till it vanishes at T_{NI}.

From Fig 2a, b, c it can be seen that the average dielectric constant $\bar{\varepsilon}$ in the nematic phase is less than the dielectric constant ε_{iso} at the transition temperature. The results are in agreement with the dielectric permittivities in strongly polar molecules reported in literature [1, 2, 5]. However, for molecules with dipole moment 2D or less the average dielectric permittivity $\bar{\varepsilon}$ is found to fall on the same straight line as in the isotropic phase reported recently [6].

From Table III it can be seen that the order parameter evaluated from dielectric anisotropy $\Delta\varepsilon = (\varepsilon_{\parallel} - \varepsilon_{\perp})$, polarizability anisotropy $\Delta\alpha = (\alpha_e - \alpha_0)$ and the dipole moment μ using Maier and Meier equation is much smaller than those obtained from refractive indices both in monotropic CPBB (μ = 5.10D), CPPOB (μ = 5.59D) and thermotropic E_4 (μ = 5.38D) liquid crystals. Thus it is clear that Maier and Meier's theory for dielectric constants in anisotropic media of strongly polar molecules ($\mu \gg$ 2D) fails to give results consistent with the experimental values. The short range antiparallel dipole correlation

TABLE III

Comparison of the order parameter S from birefringence and dielectric data

Sample	Temp. [°C]	Order parameter from birefringence		Order parameter from Maier and Meier's equation
		Neugebauer's	Vuks	
CPBB	35	0.61	0.62	0.36
	36	0.60	0.60	0.35
	38	0.56	0.57	0.34
	40	0.52	0.52	0.32
	41	0.49	0.48	0.30
CPPOB	66	0.57	0.59	0.33
	70	0.52	0.54	0.31
	73	0.49	0.50	0.30
	75.5	0.45	0.45	0.31
	76	0.43	0.43	0.31
MIXTURE E_4	38	0.64	0.65	0.23
	40	0.63	0.64	0.23
	45	0.60	0.61	0.22
	50	0.56	0.56	0.21
	55	0.50	0.50	0.18

in strongly polar nematics as proposed by Madhusudana and Chandrasekhar [11], causes a large decrease in $\varepsilon_{\parallel}$. This reduction in $\varepsilon_{\parallel}$ in molecules with dipole moment up to 2D is not much and the Maier and Meier equation could be usefully applied for evaluating order parameter as was reported recently [6].

The pretransitional effects in dielectric permittivity in the liquid crystals under study are shown in Fig. 3a, b, c when temperature dependence of dielectric permittivity ε_{iso} over wide range of temperature is illustrated. It can be clearly seen that there is a peak in

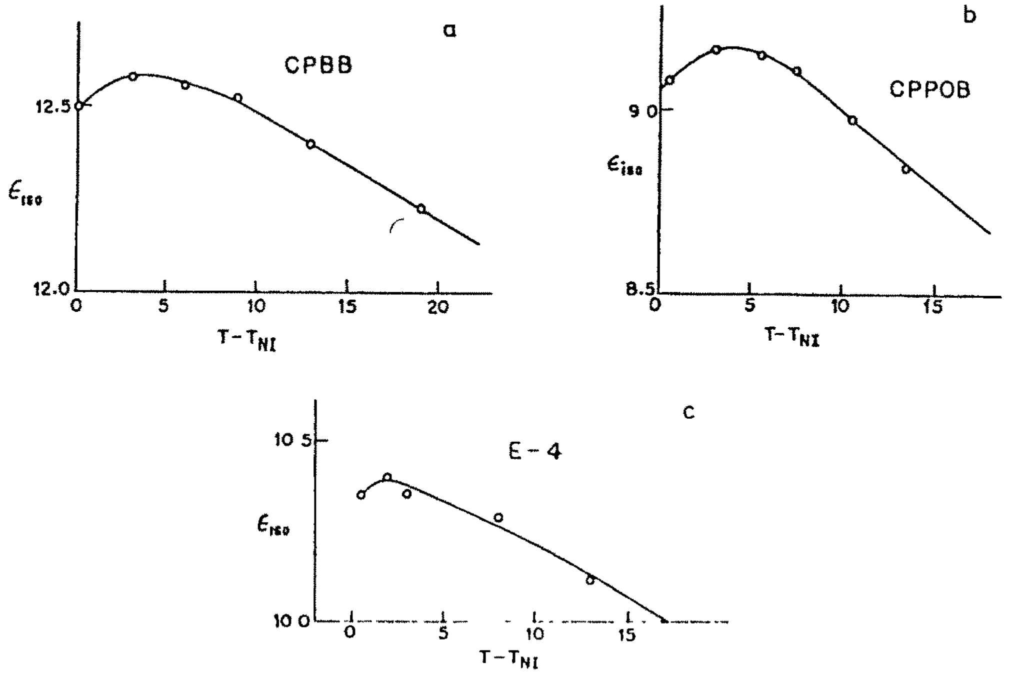

Fig. 3a, b, c. Plots of dielectric permittivities at isotropic phase vs $T-T_{\text{NI}}$

ε_{iso} value a little above the transition temperature T_{NI}. Similar pretransition effects in dielectric constants in nematics with Cyano end groups were reported by Bradshaw and Raynes [12] and Thoen and Menu [13]. Normally the ε_{iso} should monotonically increase with decrease of temperature in proportion to μ^2/kT up to the transition temperature T_{NI}. But instead, a maximum in ε_{iso} is observed, a little above T_{NI} and then decreases as T_{NI} is approached. The reduced contribution to dielectric permittivity ε_{iso} from dipole moment μ is attributed to apparent reduction in μ values due to the formation of dimers in anti-parallel local ordering [14]. The pretransition in ε_{iso} near T_{NI} showing a maximum may be due to appreciable concentration of dimers in a dynamic monomer-dimer equilibrium.

We thank Prof. S. B. Roy for his guidance.

REFERENCES

[1] M. Schadt, *J Chem. Phys.* 56, 1994 (1972)

[2] B. R. Ratna, R. Sashidhar, *Pramana* 6, 278 (1976).

[3] W. H. de Jeu, Th. W. Lathouwers, *Z. Naturforsch.* **29a**, 905 (1974).

[4] W. H. de Jeu, Th. W. Lathouwers, *Z. Naturforsch.* **30a**, 79 (1975)

[5] S. Sen, P. Brahma, S. K. Roy, S. B. Roy, *Acta Phys. Pol* **A65**, 47 (1984)

[6] K. Kali, S. Sen, S. K. Roy, *Bull. Chem. Soc. Jpn* **58**, 3576 (1985).

[7] W. Maier, G. Meier, *Z Naturforsch.* A16, 262 (1961).

[8] H F. J. Neugebauer, *Canad J. Phys.* **32**, 1 (1954).

[9] M. F. Vuks, *Opt Spektrosk.* **20**, 361 (1966).

[10] I. Haller, H A Huggins, H. R. Lilienthal, T R. McGuire, *J. Phys. Chem.* 77, 950 (1973)

[11] N. V. Madhusudan, S Chandrasekhar, Proc. Int. Conf. Liq. Cryst., Bangalore 1973, p. 427

[12] M. J. Bradshaw, E. P. Raynes, *Mol. Cryst. Liq. Cryst.* **L72**, 73 (1981).

[13] J. Thoen, G. Menu, *Mol Cryst. Liq. Cryst.* **76** (1983).

[14] L. Longa, W. H. de Jeu, *Phys. Rev.* **A26**, 1632 (1982).

[15] S. P. Tay, J. Crossley, *Canad. J. Chem.* 50, 2031 (1972).

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SPECTROSCOPIC STUDY OF PHASE TRANSITION IN *p,p'*-DI-SUBSTITUTED BIPHENYL SYSTEM

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The photo-kinematical approach was utilized previously for the investigation of solid-solid phase transition of a large number of organic molecular crystals. This method has been employed for the investigation of solid-smectic-nematic-isotropic phase transition in some *p,p'*-di-substituted biphenyl molecules In this method the luminescence intensity changes sharply in response to the phase change of the host molecule The results obtained by this method closely correlate with those obtained by other methods

PACS numbers 64 70 Md

1 *Introduction*

Liquid-crystalline materials generally exhibit [1–6] solid-crystalline polymorphism. There are a number of methods for the investigation of solid- and liquid-crystalline polymorphism, of which diffraction of X-rays [7–10], infrared and Raman spectroscopies [11], differential thermal analysis (DTA), and differential scanning Calorimetry (DSC) techniques [12–14] are widely employed Recently Ghoshal et al. [15] used a simple spectroscopic method, 'photokinematical approach' as the method has been termed, for the investigation of solid-solid phase transitions over a continuous range of temperature for a large number of organic molecular crystals. In this method, ketone molecule with high phosphorescence quantum yield is embedded as guest in the host molecular crystal, which undergoes phase transitions with change of temperatures. The changes in the intensity of phosphorescence emission from ketone with change of temperatures are monitored continuously.

It is known that in a polymorphic crystal maximum unpacking and repacking of the crystal lattice occurs at the phase transition temperatures. So, at the phase-transition temperature (T_c) the system is in a state of maximum disorder and at this temperature fluorescent state of the guest molecule is deactivated mainly by collisional nonradiative decay mechanism, producing minimum intensity. On the other hand, the temperatures (called optimum temperature, T_{op}) at which the crystal exists in stable form, are indicated by the appearance of the peaks (i e. maximum intensity) because the rigidity of the crystal cage enhances the luminescence. From the analysis of the results the transition temperatures and optimum temperatures are determined

It is known that raising of the temperatures of any liquid crystal sample results in progressive destruction of molecular order So with the increase of temperature of the liquid crystal, sharp fall of emission of guest molecule embedded in the liquid crystal host is expected at the phase-transition points.

The object of the present investigation is to find out if the same spectroscopic method may be applied to ascertain the solid and liquid crystalline phase transition points. However, in the cases where phase transitions occur at room temperature (300 K) or above, monitoring of phosphorescence intensity in the whole temperature range over which the substance exists either in solid or liquid crystalline state, is not feasible because molecules generally do not phosphores at room temperature and above. That is why it was decided to study the temperature variation of the fluorescence intensity of a suitable guest embedded in liquid crystal hosts For this purpose, tetracene molecule having a moderately large fluorescence quantum yield in the entire temperature region over which phase transition was studied, was chosen as guest.

It has been hoped that from analyses of the results on the variation of fluorescence intensity with temperature it would be possible to ascertain the phase changes of the liquid crystals and to find out the temperatures at which such phase changes take place and get some information about the molecular order at the transition points The results obtained and their discussion form the subject of the present paper

2. *Experimental*

The liquid crystals studied in the present investigation are K$_{15}$. *p*-cyano-*p*′-*n*-pentylbiphenyl, M$_{15}$, *p*-cyano-*p*′-*n*-pentoxybiphenyl and K$_{24}$, *p*-cyano-*p*′-*n*-octylbiphenyl and *p*-cyanophenyl-*p*-butylbenzoate The first three compounds were obtained from BDH, England and the fourth one from Eastman Kodak Company, U.S.A The samples were used for investigation without further purification Tetracene, from Sigma Chemical Company, U.S.A., was purified by recrystallization and used as a guest molecule in the liquid-crystal hosts A solution of concentration $10^{-5}/10^{-6}$ M was prepared by dissolving a very small measured amount of tetracene in liquid crystal brought to isotropic phase by gentle heating The solution was transferred in a quartz sample tube 3 mm diameter and inserted in a quartz dewar of Perkin Elmer MPF 44A fluorescence spectrophotometer. A copper constantan thermocouple junction was introduced in the solution to record its temperature.

Complete fluorescence spectra of the guest tetracene in the different liquid crystal solutions were recorded at room temperature with the spectrophotometer in the usual manner and the wavelength (λ_{max}) of maximum fluorescence intensity was determined. The emission monochromator was set at this wavelength in all succeeding experiments Liquid nitrogen was poured into the dewar and the solution was rapidly frozen into a solid mass. The intensity of emitted fluorescence at the wavelength selected was monitored continuously while the sample temperature increased progressively from 77 K to 300 K due to evaporation of liquid nitrogen The gradual change in sample temperature was simultaneously recorded at regular interval of few degrees on the chart paper by means of a marker. Fluorescence intensity versus temperature curve was then plotted for the study of phase transitions For obtaining the intensity — temperature curve at temperature higher than 300 K, the samples were heated by blowing hot air inside the quartz dewar Measurements for every sample were repeated at least three times to obtain consistent results. The accuracy in the measurements of the transition points is ±1 K

3 *Results and discussion*

The full fluorescence spectra of tetracene guest in different liquid crystal hosts at room temperature are shown in Fig 1 Emission wavelength is fixed at maximum intensity (λ_{max}) position of the fluorescence spectrum (I_F) The characteristic plots of the fluorescence intensity (I_F) versus temperature (T) in K for four liquid-crystalline materials are presented in Fig. 2.

The T_c and T_{op} values and the temperatures (T_T) at which the sharp fall in intensity occurs, are given in Table I. T_T approximately correspond to the liquid-crystalline phase transition temperatures as reported by the chemical companies. Reported values are also given in Table I.

It is seen from Fig. 2 that I_F-T curve for K_{24} displays three distinct peaks at 239, 285.5 and 296 K and minima at 230, 276 and 290 K. Besides these maxima and minima, I_F is found to fall sharply at temperatures 306 and 313 K The temperature 296 K approximately corresponds to the crystal nematic phase transition temperature 295 K as supplied

TABLE I

Values of transition temperatures of various samples

Compounds	Temperatures corresponding to different phase transitions in K K → K					
	T_c	T_{op}	K → N	K → S	S → N	N → I
K_{24} *p*-cyano-*p'*-*n*--octylbiphenyl	230(I–II) 276(II–III) 290(III–IV)	$77 < (I) < 230$ 239(II) 285(III) $290 < (IV) < 296$		296 (295)	306 (307)	313 (304)
K_{15} *p*-cyano-*p'*-*n*--pentylbiphenyl	214(I–II) 293 5(II–III)	$77 < (I) < 214$ 235(II) $293\ 5 < (III) < 296\ 5$	296 5 (296 5)			308 (308 5)
M_{15} *p*-cyano-*p'*-*n*--pentyloxybiphenyl	203(I–II) 305(II–III)	$77 < (I) < 203$ 230(II) 310(III)	320 (321)			339.5 (340,5)
p-cyanophenyl-*p*--butylbenzoate				308		315.5 (314 5)

Data within the brackets are reported values. K — crystal, N — nematic, S — smetic, I — isotropic.

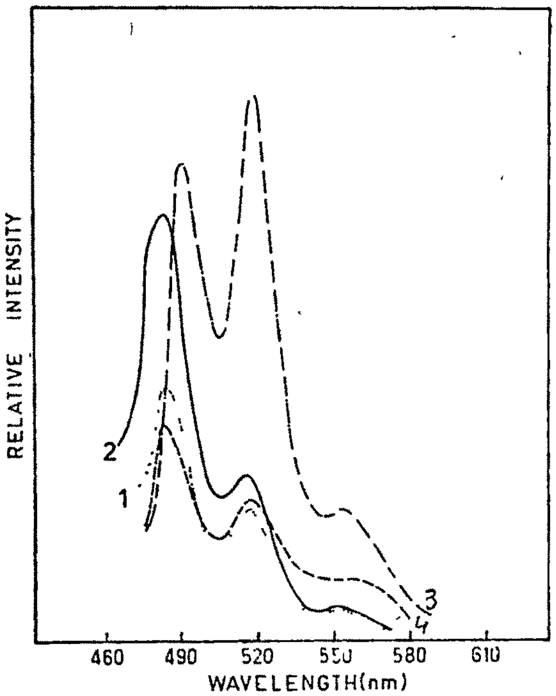

Fig. 1. Full fluorescence spectra of tetracene in K_{24} — *1*, K_{15} — *2*, M_{15} — *3* and *p*-cyanophenyl *p*-butylbenzoate — *4*

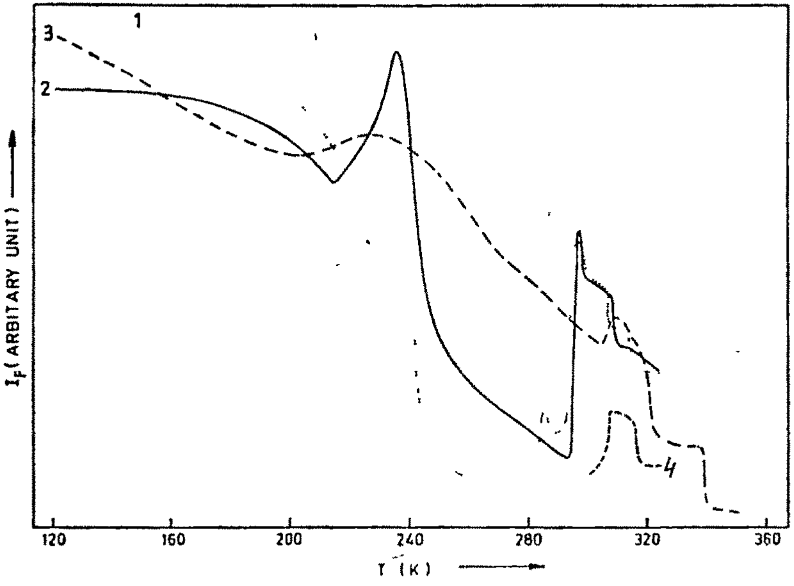

Fig. 2. Temperature dependence of fluorescence intensity (I_F) of guest tetracene in K_{24} — *1*, K_{15} — *2*, M_{15} — *3* and *p*-cyanophenyl *p*-butylbenzoate — *4*

by the chemical company. The occurrence of well-defined maximum at this temperature is noteworthy. According to Ghoshal et al. [15], the peaks at 239 (form II) and 285.5 (form III) are due to the formation of two different crystalline polymorphs of the sample K_{24} at these temperatures and the minima at temperatures 230, 276 and 290 K are due to the transitions between the crystalline forms I (which exists between 77 and 230 K) and II, II–III and III–IV (which exists between 290 and 296 K) respectively. At 290 K the solid system is in a state of maximum disorder due to which minimum fluorescence intensity of the guest molecule is observed As the temperature is raised from 290 K, further repacking of crystal starts as a result of which I_F begins to increase but before coming to any stable crystalline form it breaks into smectic liquid crystal at 296 K and intensity (I_1) begins to decrease, resulting in a maximum in I_F-T curve at crystal-smectic transition temperature. Smectic → nematic and nematic → isotropic phase transition temperatures of K_{24} as supplied by the chemical company, 307 and 314 K, respectively, approximately correspond to the temperatures 306 and 313 K where sharp fall in I_F was observed

Maximum in the I_F-T curve is also observed by K_{15} in the crystal-nematic transition temperatures 296.5 K and sharp fall at nematic-isotropic transition temperature 308 K Maximum at 235 K is due to some stable crystalline form (II) and the minima at 214 and 293.5 K correspond to the transition between the crystalline forms I (which exist between 77 K and 214 K) — II and II–III (which exists between 293 5 and 296 5 K)

The I_F-T curve for M_{15}, by contrast, shows a distinctly different behavior at crystal-nematic transition temperature 320 K Instead of peaks, as observed in the crystal-liquid crystal transition temperature in K_{15} and K_{24}, only sharp fall in emission intensity is observed in the crystal-nematic transition temperature in M_{15} Maxima observed at 230 and 310 K are due to two polymorphic forms II and III, respectively, and minima at 203 and 305 K are due to the transitions between the solid polymorphic forms I (which exists between 77 and 203 K) — II and II–III, respectively At 310 K the solid assumes a stable crystalline form (III) and provides an optimum environment for the large fluorescence emission from the trapped tetracene molecule as evidenced from the appearance of the peak in I_F-T curve at this temperature As the temperature is raised from 310 K, unpacking of the lattice i.e. disorder of the system increases causing lowering of emission intensity and as it reaches at 320 K (i e at crystal-nematic transition temperature) a sudden increase in the disorder of the system occurs causing a sharp fall in fluorescence Again sharp fall in intensity is observed with the increase of temperature at 339.5 K which approximately corresponds to the nematic-isotropic transition temperature 340.5 K.

P-cyanophenyl-*p*-betyl benzoate shows liquid-crystalline mesophase only during cooling. So, in this case, sample was first heated to 350 K and then allowed to cool down to room temperature and during cooling emission intensity was monitored as a function of temperature. The I_F-T curve is shown in Fig. 2 Sharp change in intensity is observed at the phase transition points. No solid-solid phase transitions were observed in the sample during heating from 77 K to room temperature

In conclusion it can be said that photokinematical approach can be used for the identification of solid- as well as liquid-crystalline phase transitions. In some liquid-crystalline samples (e.g K_{15} and K_{24}) just before the formation of liquid-crystalline mesophase from crystal there occurs repacking of the lattice structure within the crystal, whereas in other case (e.g. M_{15}) just before breaking into nematic form, unpacking of the lattice structure within the crystal occurs.

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REFERENCES

[1] K. Z. Ogorodnik, *Acta Phys. Pol.* A55, 935 (1979)

[2] S Venugopalan, J R Fernandes, G V Vani, *Mol. Cryst. Liq. Cryst* 31, 29 (1975)

[3] B. J. Bulkin, K. Berzinsky, T. Kennelly, *Mol Cryst Liq Cryst* 55, 53 (1979)

[4] M. Sorai, T. Nakamura, S Seki, Proc. Int Conf. on Liquid Crystals, Bangalore 1973; *Pramana,* Suppl. 1, 503 (1973)

[5] V. G Vhide, S. A. Agnihotry, S. Chandra, *Indian J. Pure Appl. Phys* 19, 821 (1981).

[6] K. S. Kunihisa, M Gotoh, *Mol Cryst Liq. Cryst* 42, 97 (1977).

[7] *Molecular structure by diffraction methods,* ed. L. E Sutton, G A Sim, The Chem. Soc. London 1976, Vol 4

[8] A. I Kitaigorodsky, *Advances in Structural Research by Diffraction Methods,* ed. R Brill, John Wiley and Sons, New York, London 1966, Vol. 3, p. 173.

[9] P. J. Wheatly, *The determination of molecular structure,* Oxford Univ. Press, 1969.

[10] G. Ferguson, J. M. Robertson, *Advances in Physical Organic Chemistry*, ed , V. Gold, Academic Press, London 1963, Vol. 1, p. 203.

[11] J. E. D. Davies, *J. Mol. Structure* 10, 1 (1971)

[12] *Differential thermal analysis,* ed R. C. Mackenzie, Academic Press, London, New York 1970

[13] J. P. McCullough, D W. Scott, *Experimental Thermodynamics* I, Butterworths, London 1968

[14] C. N. R Rao, K J Rao, *Phase Transitions in Solids*, McGraw-Hill, 1978.

[15] S. K. Ghoshal, S. K Sarkar, G. S Kastha, *Mol Cryst Liq Cryst* 91, 1 (1983)

REFRACTIVE INDICES, DENSITY AND ORDER PARAMETER IN A NEMATIC LIQUID CRYSTAL

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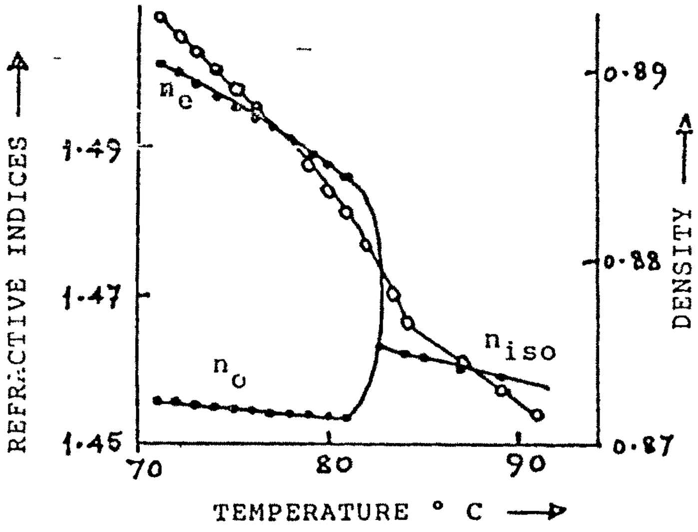
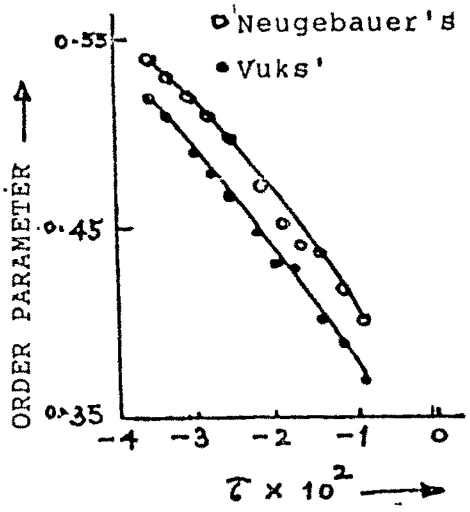
The most important parameter of a liquid crystal governing almost all the physical properties is its order parameter. The temperature variation of refractive indices, density and order parameter for a nematic liquid crystal Trans-trans-4'-heptylbicyclohexyl-4-carbonitrill (CCH-7) has been reported here. The observed transition temperatures are as under:

$$\text{Crystal} \overset{71^\circ\text{C}}{\longleftrightarrow} \text{Nematic} \overset{83^\circ\text{C}}{\longleftrightarrow} \text{Isotropic}$$

Abbe refractometer having the temperature accuracy of ±0.1 °C is used/1/ for the measurements of refractive indices n_e and n_o in the nematic phase and n_{iso} in isotropic phase. The densities are measured by a standardised picnometer.

Fig. 1 shows the temperature variation of n_e, n_o, n_{iso} and ρ. The observed jump in density at the I → N transition indicates a first order transition. The order parameter is computed by using Vuks'/2/ and Neugebauer's/3/ models. Fig. 2 shows the variation of order parameter with temperature in the nematic phase. Both above approaches indicate the order parameter to be comparable. The two approaches being based on entirely different assumptions of local fields, it is not essential them to lead to exactly the same value of the order parameter. Besides, the calculation of $(\alpha_\parallel - \alpha_\perp)$ by the extrapolation technique/4/ has the limitation of 10%.





References : /1/. S. Sen, K. Kali, S.K. Roy and S.B. Roy, M.C.L.C., 126, 269, 1985. /2/. M.F. Vuks, Optics and Spectro., 18, 292, 1950. /3/. H.E.J. Neugebauer, Canad. J. Phys., 18, 292, 1950. /4/. I. Haller, H.A. Higgins, H.R. Lilienthal and T.R.McGuire, J. Phys. Chem., 77, 950, 1973.

PHASE TRANSITION STUDIES IN A NEMATIC LIQUID CRYSTAL : OBP

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The present paper contains the ultrasonic velocity and specific volume measurements in nematic and isotropic phases of the liquid crystal P-Octyloxybenzylidine-p-Phenetidine (OBP). OBP has following transition temperatures :

$$\text{Crystal} \xleftrightarrow{91^\circ\text{C}} \text{Nematic} \xleftrightarrow{117^\circ\text{C}} \text{Isotropic}$$

The temperature dependence of ultrasonic velocity (V) at 2 MHz and specific volume (v) were measured by Rao and Rao method/1/ and a special dilatometer/2/ respectively which are displayed in the figure.

In the vicinity of phase transition, the ultrasonic velocity suddenly decreases in the isotropic phase, then increases in the nematic phase with decrease in temperature. The anomalous decrease is ≃ 2.2% in comparison to the normal linear temperature dependence of velocity. The observed change in the velocity at the isotropic - nematic transition results from the disordered molecular arrangement in the isotropic phase to an ordered arrangement of the molecules in the nematic phase, with long range orientational order.

The jump in the specific volume, $\Delta v/v \simeq 0.21\%$, indicates a first order phase transformation at the isotropic-nematic transition. The order parameter Sk/3/ is found to be 0.437 and is in accordance with the theoretical predictions.

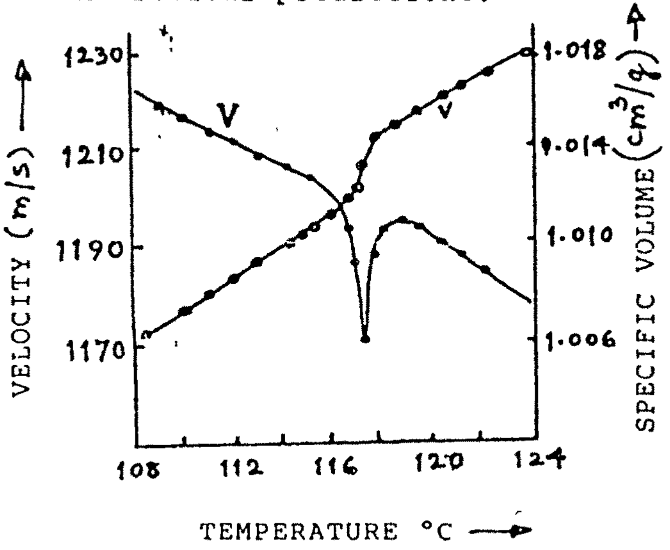

Fig:
Temperature dependence of ultrasonic velocity (V) and specific volume (v).

References:
/1/. K.S. Rao and B.R. Rao, J. Sci. Ind. Res., 16B, 483, 1957.
/2/. A.K. George, R.A. Vora and A.R.K.L. Padmini Acustica, 47, 149, 1981.
/3/. W. Maier and A. Saupe, Z. Naturforsch, 14a, 882, 1959.